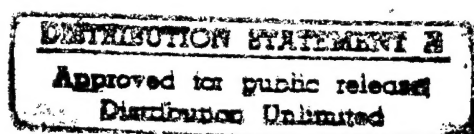
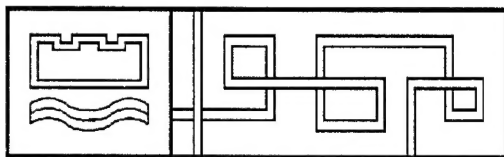


12<sup>th</sup> Bratislava International IUPAC/EPF Conference on Polymers



**MODIFIED POLYOLEFINS  
FOR ADVANCED POLYMERIC MATERIALS**

**Proceedings**



August 25-28, 1997  
Bratislava, Slovak Republic

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## **PROCEEDINGS**

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### **MODIFIED POLYOLEFINS FOR ADVANCED POLYMERIC MATERIALS**

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## INTRODUCTION

This Proceedings cover the abstracts of contributions arranged as Main Lectures (ML), Contributed Lectures (CL) and Posters (P) with the numbers identical to those in the Programme of

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held in the Congress Center of Foreign Affairs, Bratislava, Slovak  
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The Organizers of the Conference welcome you in Bratislava with the hope that the Proceedings will contribute to the stimulation of the discussion and to your further scientific work.

The Organizing Committee

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## ML-1

### NOVEL POLYOLEFIN MATERIALS PREPARED VIA CATALYSIS AND REACTIVE PROCESSING

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Since the discovery of the catalytic low pressure olefin polymerization during the 1950's, remarkable progress has been made in polyolefin technology. Today highly active and stereoselective catalyst generations produce tailor-made polyolefins in gas phase and liquid pool processes, thus eliminating the need for hydrocarbon diluents as well as removal of catalyst residues and by-products, e.g., waxes and low stereoregular polymer fractions. As hydrocarbon resins polyolefins retain oil-like energy content and are readily recycled. Upon thermal cleavage at temperatures above 400°C, synthetic crude oil can be recovered in feedstock recycling and combustion processes. Due to its attractive combination of low price, wide property and application range, the environmentally friendly polypropylene is competing very successfully with other polymeric materials.

In principle, since the 1950's polyolefin catalyst and process development has been revolutionized every fifteen years. Progress in the development of magnesium halide supported catalysts has led to novel reactor blend technology where multiphase polypropylene are produced in staged reactor systems. In a gas phase polymerization EPM rubber or poly(styrene-co-maleic anhydride) can be incorporated into micropores of spherical polypropylene (Catalloy® and Hivalloy® processes from Montell). In recent years single-site metallocene catalysts have emerged which give excellent control on olefin homo- and copolymerization. As a function of the metallocene structure it is possible to control molar mass, end groups, stereochemistry, comonomer incorporation, and morphology independently without sacrificing narrow molar mass distributions. In addition to isotactic polypropylene also syndiotactic, hemiisotactic and stereoblock polypropylenes are available in high yields. Regio- and stereoselectivity of the catalysts, affording head-to-head and 1,3-insertion as well as stereoirregularities which are randomly distributed along the isotactic polypropylene chain, give control of polypropylene crystallization which depends primarily upon the average length of isotactic segments between two steric defects. Highly optically transparent polypropylene, crystallizing in  $\gamma$ -modification, can be produced. Metallocene



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catalysts are of special interest in olefin copolymerization where comonomer incorporation is feasible over the entire composition range with very uniform comonomer distribution. Today molecular modeling can be used to predict performance of metallocene catalysts in ethylene copolymerization. When 1-olefin comonomer incorporation in the polyethylene backbone exceeds 10%, chain folding is prevented and fringed micelle-type nanostructures are formed. Commercial examples of ethene/1-olefin copolymers are Affinity<sup>®</sup> and Engage<sup>®</sup> product lines of Dow and Luflexen<sup>®</sup> from BASF AG. Also cycloolefins can be copolymerized with ethylene to produce amorphous and semicrystalline optically transparent engineering plastics with heat distortion temperatures above 150 °C, thus expanding the application range of hydrocarbon resins in engineering applications. Cycloolefin copolymers such as Topas<sup>®</sup> from Hoechst are expected to find applications in compact disk and medical packaging markets.

While incorporation of polar monomers is limited in the case of group IV transition metal catalysts due to severe catalyst poisoning, group VIII (Ni, Pd) catalysts tolerate known catalyst poisons such as carbon monoxide. Strictly alternating ethylene/CO copolymers, containing a few percent of propene comonomer, such as Shell's Carilon<sup>®</sup>, melt at 220°C and exhibit polyamide 6-like properties and excellent barrier properties. With diimine complexes of nickel and palladium methacrylate and other vinyl-functional esters can be incorporated into polyethylene. Due to the chain migration mechanism, which has been found during the 1980's by Fink and Bayer AG, the resulting polyethylenes are highly branched. The degree of branching can be controlled by means of pressure and temperature. Branched polyethylene (Versapoi<sup>®</sup>) are being developed by Du Pont. New catalyst generations tolerating polar monomers will facilitate better utilization of readily available petrochemical feedstocks.

In addition to catalyst and process technologies, polymer processing will continue to play an important role in diversification and up-grading of commodity polyolefin materials via chemical modification during processing using extruders as reaction vessels. Since the 1960's special reactive processing technologies have been introduced to functionalize polyolefins, to control rheology by means of controlled degradation, and to improve adhesion and compatibility with other materials. Reactive blending is the method of choice to achieve novel polymer property combinations without requiring novel polymerization processes. The potential for morphology control and improvement of toughness/stiffness balance was demonstrated for rubber modified polypropylene/polyamide 6 blends.

## ML-2

### PROCESSING OF INTRACTABLE POLYETHYLENES

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Polyolefins are the most important class of present-day thermoplastic polymers and constitute over 50% of the total synthetic polymer production. Polyolefins may at first sight appear to be rather low-tech and well-established polymers (plastics), comprising a full range of types and subtypes, tailored for the end-user and well-defined application areas.

However, the field of polyolefins is, after the discovery of the stereospecific polymerization of olefins by Ziegler and Natta in the mid-1950s, once again in a revolutionary stage due to the introduction of metallocene catalysis. Novel types of polyolefins are produced nowadays, comprising very low density polyethylenes (plastomers) and syndiotactic polypropylenes.

Apart from sophisticated chemistry, various physical methods have been developed to enhance the processing characteristics and performance of polyolefins. A few examples will be presented concerning processing of ultra-high molecular weight polyethylene, UHMW-PE.

UHMW-PE is a linear polyethylene grade possessing, according to ASTM definitions (D4020), a molar mass of at least  $3.000 \times 10^3$  kg/mole. UHMW-PE is well known for its abrasion resistance and excellent wear characteristics. UHMW-PE is potentially an excellent engineering plastic but due to its extremely high melt viscosity, this polymer is considered to be intractable. In practice, UHMW-PE is supplied as a reactor powder and processed via compression-moulding sintering. Via machining of the semi-finished stock, various products can be made such as linings, ski facings and artificial hip-joints.

Various routes have been developed to improve the processing of UHMW-PE including solvent, reactive solvents (monomers) and processing via the hexagonal phase.

#### 1. Processing with Solvents

Solution-(gel) spinning of UHMW-PE is used to produce high-performance polyethylene fibers possessing specific stiffness and strength values over respectively, 100 and 4 Gpa. Some recent developments will be discussed concerning novel applications and product improvements.

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## 2. Processing with Reactive Solvents (Monomers)

The use of solvents in processing intractable polymers has the intrinsic disadvantage that all solvent has to be recycled again in view of environmental legislation. However, when reactive solvents (monomers) are used, the solvent could be incorporated in the product after preprocessing (1). Some examples will be discussed.

## 3. Processing via the Hexagonal Phase, the concept of Monomolecular Crystals

UHMW-PE is usually obtained via polymerization of ethylene at relatively low temperatures. If the polymerization temperature  $T(\text{pol})$  is below the dissolution temperature  $T(\text{diss})$ , the growing polymer chain will crystallize during polymerization. In this way, polymer crystals will be obtained consisting, in the limit, of one polyethylene molecule, viz. monomolecular crystals. The so-called Triple-point Q of these UHMW-PE grades is rather low and processing via the hexagonal phase becomes feasible (2).

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## MISCIBILITY OF CRYSTALLINE AND AMORPHOUS POLYMERS: POLYETHYLENE/POLYISOBUTYLENE BLENDS

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Polymer blends are used in large quantities in all fields of application. Although the best known examples of commercial products are materials like Noryl and Bayblend, blends are frequently prepared also from commodity thermoplastics as well. Polypropylene is modified with EPDM elastomer in order to prepare impact modified PP for bumpers and polyethylene is blended with atactic polypropylene, polyisobutylene or other elastomers to prepare films for packaging purposes. The study of the miscibility/structure/property correlations of such blends is of large theoretical and practical importance.

Miscibility of components determine the structure of the blend, which on the other hand, has a pronounced effect on properties. Numerous methods exist for the estimation of miscibility, the determination of the glass transition temperature is probably the most often used approach. In amorphous polymers  $T_g$  can be determined with various techniques, including thermal analysis (DSC), dynamic mechanical (DMTA) or dielectric spectroscopy, etc. The determination of  $T_g$  and miscibility in polyolefin blends is very difficult, shown also by the very limited number of miscibility data for these polymers. In the case of PE, the opinions differ even on the glass transition temperature, values between  $-120^\circ\text{C}$  and  $+70^\circ\text{C}$  are reported in the literature [1-3]. The source of these difficulties is the crystalline structure of the polymer, its apolar character leading to the lack of specific interactions and the ill defined, broad transitions detected in it by most methods.

In this study an attempt was made for the determination of miscibility in polyethylene/polyisobutylene (PE/PIB) blends. The Flory-Huggins interaction parameter was determined from glass transitions temperatures by a modified version of the approach introduced by Kim and Burns [4]. The original technique requires the knowledge of the  $T_g$  of both components. Since the  $T_g$  of PE cannot be determined by DSC, the values were deduced from the changes in the specific heat of PIB. Good agreement was found between the interaction parameters obtained from the two independent methods. The magnitude of the parameters indicate that even dispersion forces can lead to sufficient interaction resulting in acceptable properties of the blends.

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## ML-4

### POLYOLEFIN SYNTHESIS AND STRUCTURES

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Polyolefins currently comprise about 50% of the polymer production and about 75% of commodity polymers, which is presently about 100 million tons per year. The major olefin polymers are polyethylene, both low density and high density, and polypropylene. Styrene and diene polymers play also an important part. Not much has fundamentally changed in the production and of the high pressure processes for polyethylene, although relative small changes in the configuration of plant reactors and in the reaction condition can modify the final products. The introduction of coordination initiators opened the way for the preparation of linear polyethylene and of crystalline, isotactic polypropylene.

Coordination polymerization allowed the tailoring of the structures and properties of polyolefins. In the case of polyethylene, the type of chain branching could be controlled by copolymerization with selected olefins. For polypropylene, the degree of tacticity, the sequence of tacticity (elastomeric polypropylene), molecular weight and molecular weight distribution can now be modified. While the initial coordination initiating systems consisted of titanium chlorides and aluminum alkyls, today's catalysts are transition metal catalysts supported on magnesium chloride, often in combination with other inert carriers. In the last decade, substantial progress has been made in the synthesis of new types of transition metal catalysts, metallocenes, not only of titanium, but, more importantly, of higher transition metals like zirconium and some rare earth metals. These catalysts have chiral cavities and, in combination with methylaluminoxanes, can be used highly effectively in solution for olefin polymerization. These systems are showing great promise but to date only few are used commercially.

Supported catalysts involving magnesium chloride and often an inert carrier allowed a significant increase of the polymerization rate and a more efficient way of utilizing the initiator leading, in the case of propylene polymerization, to the 4th generation of "catalysts", initiating systems, where the transition metals are separated and where nearly each site can grow a polymer chain.

Most processes today function without solvents and produce polymer particles which can be used directly for extrusion and injection molding. The technical problem is the dissipation of the heat of polymerization.

Some of the new initiating systems allow the preparation and the potential of commercialization of such polymers syndiotactic polypropylene and syndiotactic polystyrene.

A new development in ethylene polymerization is the use of ruthenium compounds as catalysts. These new polyethylenes are highly branched polyethylene and are formed with continuous rearrangement during the polymerization.

The chemical structure of polyolefins: molecular weight, molecular weight distribution, chain branching, distribution of chain branches, stereochemistry of the monomer units in the polymers, influence significantly and even determine their morphology. While linear polyethylene normally crystallizes in a zig-zag conformation but in a folded chain structure, polypropylene crystallizes, in addition, in a helical  $3_1$  helix with a repeat distance of  $6.65 \text{ \AA}$ . These three fold helices consist of half and half left- and right-handed helices. Small variations of the positions of the left and right-handed helices in the crystal unit cell lead to the three phases that are known for polypropylene, the  $\alpha$ -,  $\beta$ -, and  $\gamma$ - phases. They are obtained by crystallization under the most favorable crystallization conditions for its phase with the proper temperature profile and nucleation for the particular phase.

## ML-5

### CHEMICAL MODIFICATION OF POLYMERIC HYDROCARBONS

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Unsaturated polymeric hydrocarbons can undergo a large number of addition reactions like hydrogenation, halogenation, epoxidation or reactions with thiols. Saturated polymeric hydrocarbons can be substituted by a large number of reagents yielding some technically useful polymers, e.g. by halogenation or chlorosulfonation. Even more important are addition reactions of saturated polymeric hydrocarbons, which will result in functionalisation for further use, e.g. by introduction of polar or chemically reactive groups. Such polymers can also be applied in polyolefin blends as compatibilizers, for grafting reactions or in reactive processing.

Hydrocarbons as polyethylene (PE) or polypropylene (PP) are incompatible with practically all other polymers and, therefore, of limited use in blends. To adjust their apolar chains to more polar blend components, the polyolefines can be provided with acrylic or maleic acid derivatives via a peroxide initiated radical grafting. Depending on the monomer, single units or short grafts are attached to the polyolefine chains. Thus modified polyolefines interact more favourably with many polymers. Side reactions due to the oxy radicals lead to chain degradation (PP) or crosslinking (PE).

Moreover, the attached functions can react with suitable groups of other polymers. Well known is the reaction of amino end groups of polyamides with maleinated polyolefines that leads to graft copolymers by a condensation mechanism of "grafting onto". These polymer-polymer coupling reactions proceed in viscous two-phase blend melts and are, accordingly, kinetically complex.

Unsaturated ethylen-propylen (EPDM) and diene rubbers, in particular polybutadiene (BR), can be modified by "grafting onto" processes, too, but also by "grafting from" processes. Many monomers are readily grafted from polyolefinic macroradicals in the course of radical bulk or solution polymerisations. Phase morphologies varying from filled rubbers to high-impact modified "salami" thermoplastics and transparent micellar systems can be intercepted in situ, in these processes. In special cases, double-grafted and block-grafted copolymers can be prepared.

## ML-6

### GAS BARRIER PROPERTIES OF POLYOLEFIN/EVOH BLENDS

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Compatibilization of low density polyethylene (LDPE)/ethylene vinyl alcohol (EVOH) (70/30 wt%) blends was investigated in terms of morphology, crystallization and melting behavior, rheological, and tensile properties. Maleic anhydride grafted linear low density polyethylene (LLD-g-MAH) was applied at various concentrations (from 1 to 12 phr). The interesting effect of compatibilization on the nonisothermal crystallization kinetics of the blends was noted, and the correlation between morphology and rheological and tensile properties was also discussed. Morphological analysis showed that the blends exhibited finer dispersion of EVOH phase when LLD-g-MAH was added. Nonisothermal crystallization exotherms of the compatibilized LDPE/EVOH blends showed the retarded crystallization of the dispersed EVOH phase, which was probably resulted from the constraint effect of the grafted EVOH (EVOH-g-LLD) as well as the size reduction of EVOH domains. The blends exhibited increased melt viscosity and storage modulus and also enhanced tensile properties with the addition of LLD-g-MAH, which seemed to be attributable to both dispersed particle size reduction and improved interfacial adhesion.

Morphology and oxygen barrier properties of LDPE/EVOH blends have been studied. Laminar dispersion of EVOH with high oxygen barrier properties was obtained in the matrix of LDPE when extruded through an annular blown film die. Various laminar morphologies were observed and the main factors determining the morphology of the blends were viscosity ratio of the components, processing conditions, and compatibilizer level. Large predeformed domains in the extruder outlet with short residence time under high screw rpm and low viscosity ratio ( $\eta_{d(EVOH)}/\eta_{m(LDPE)}$ ) in the die favored the formation of well-developed laminar structure. Increasing the amount of compatibilizer (LLD-g-MAH) yielded a larger number of thinner EVOH layers, which was resulted from lower interfacial tension yielding smaller predeformed EVOH domains in larger numbers and favoring the deformation of EVOH domains. Preblending LLD-g-MAH with LDPE produced more and thinner layers compared with preblending LLD-g-MAH with EVOH, which was due to the affinity difference of LLD-g-MAH to LDPE and EVOH. Morphological changes of the LDPE/EVOH blends were explained by consideration of the EVOH layer size ( $L \times R$ ) and the number of EVOH layers ( $N$ ), which were closely related to predeformed domain size ( $L_o \times R_o$ ). High Weber number (resulted from large  $L_o \times R_o$  and low interfacial tension) and low viscosity ratio ( $\lambda$ ) increased deformability of the EVOH droplets, yielding large  $L \times R$ . However, small  $L_o \times R_o$  produced high  $N$ . In the uncompatibilized blends,  $(L \times R) \times N$  increased as  $L_o \times R_o$  increased if  $\lambda < 1$ . In the compatibilized blends, enhanced deformability of EVOH domains and higher  $N$  due to smaller  $L_o \times R_o$ , both resulted from lower interfacial tension, yielded higher  $(L \times R) \times N$ . With 6 phr of the LLD-g-MAH (here,  $L_o \times R_o \cong 60 \mu m^2$ )  $(L \times R) \times N$  showed maximum value ( $\cong 63000 \mu m^2 / 100 \mu m$ ), resulting in the highest oxygen barrier property ( $P_{LDPE} / P_{blend} \cong 740$ ). Oxygen permeability of the LDPE/EVOH blends was closely related to the morphological changes which were described by  $(L \times R) \times N$ . As expected, oxygen permeability decreased as  $(L \times R) \times N$  increased. It is shown that  $(L \times R) \times N$  can be a useful indicator of the oxygen barrier properties of the LDPE/EVOH blends.

Properties of blends having two types of hybrid dispersed phases as laminar morphology were investigated. The hybrid dispersed phases were respectively prepared from dry blending of EVOH and



nylon6(*E+N*) and melt blending of EVOH and nylon6(*E/N*). Oxygen and toluene barrier properties of the blends were interpreted in terms of morphological changes (number and size of layers) and differences in barrier properties of the hybrid dispersed phases themselves. One hybrid dispersed phase (*E+N*) consisted of simple sum of EVOH and nylon6 existing separately in LDPE matrix. Oxygen barrier properties of the blends having the *E+N* hybrid dispersed phases were found to be linearly dependent on EVOH portion in the *E+N* hybrid dispersed phases but toluene barrier properties of the blends exhibited negative deviation. Linear dependence of tensile properties on the relative portion of the components in the *E+N* hybrid dispersed phases was also observed. The other hybrid dispersed phase (*E/N*) seemed to form a new dispersed phase having different properties from EVOH and nylon6. Compared to the blends having the *E+N* hybrid dispersed phases, positive deviations in both oxygen and toluene barrier properties of the blends were observed, which was believed to be resulted from favorable morphological changes and comparable barrier properties of the *E/N* hybrid dispersed phases themselves. Tensile properties of the blends also showed positive deviation.

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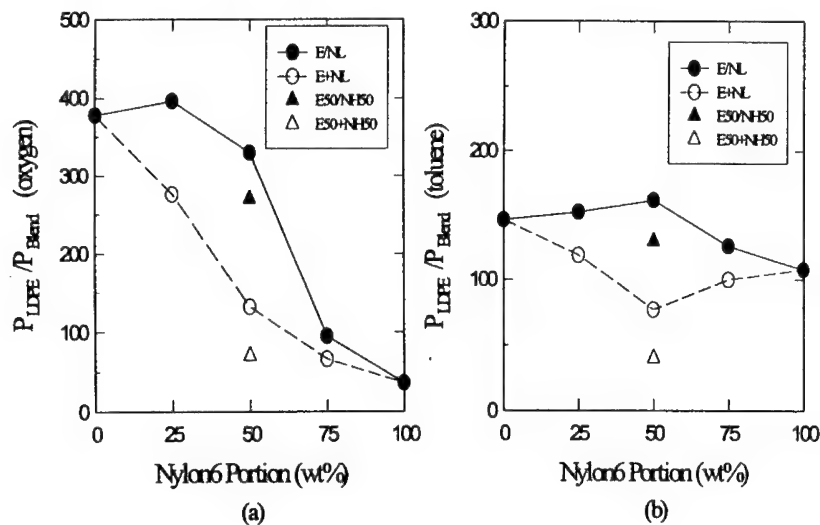


Fig. Oxygen and toluene barrier properties of LDPE/(*E+N* or *E/N*)/LLD-g-MAH  
(= 74.1/18.5/7.4 wt%) blends

- (a) Oxygen barrier properties vs. relative nylon6 portion in the hybrid dispersed phase  
(b) Toluene barrier properties vs. relative nylon6 portion in the hybrid dispersed phase.

**ML-7**

## **CHALLENGES IN PP BY CHEMICAL MODIFICATION**

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Radical reactions of i-PP are a well known technical process for the chemical degradation to increase the flowability of the i-PP melt. By decreasing the temperature and increasing the life time of the PP-radicals, a process to build long chain branched i-PP, was developed. The long chain branched-i-PP allows to introduce the i-PP in processing technologies as blow moulding film technology or foaming technology. The mechanism will be discussed.

The radical grafting of Polypropylene (PP) becomes more important for the developing of PP-alloys with extended properties. We polymerize and graft MMA and Styrene in PP in solid state at low temperatures. Grafting and polymerizing in solid state means solving the monomers in the PP-powder directly from the reactor without contacting with oxygen (air). The reaction is started by the decomposition of a peroxide. The reactivity of the primary radicals from the peroxide and the transfer reactions of the polymer radical of the PMMA or PS influenced the amount of the grafted second polymer. We measured the solubility of the monomers and the peroxide in the amorphous i-PP-phase. The grafting yield and the dispersity of the second polymer depends on the solubility or dispersity of the peroxide and the monomers in the PP-powder particles.

The experimental results show a grafting yield > 50 % for both monomers with average molecular weights  $M_w > 500.000 \text{ g/mol}$ .

The high polymerization rate and the conversion near 100 % give us the information to a divergent mechanism in comparison to the homo polymerization of Styrene or MMA in absence of PP. The difference in the polymerization reaction can be well understood in the termination step with a hindered mobility of the polymer radical chain ends.

So, we have to describe the termination reaction as a mechanism in a diffusion hindered medium of the polymer radicals. R.C. Schulz /1/, Buback et. al. /2,3/

and Kiparissides et.al. /4/ give an equation to describe the  $k_t$ -value in a diffusion controlled medium:

$$k_t = \frac{k_{t0}}{1 + \frac{r_i^2}{3} \cdot \frac{\lambda_0}{D} \cdot k_{t0}} + A \cdot k_p \cdot M$$

for  $D \rightarrow 0$  for polymers follows

$$k_{tD0} = A \cdot k_p \cdot M$$

with  $A = \frac{\text{CRD}}{\text{Cm}^0}$  a reaction diffusion coefficient

By using the  $k_t$ -values in the equation for the all over polymerization rate we get a good correlation between calculation and experimental results.  
The properties and applications of the PP-alloys will be discussed.

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ML-8

## MOLECULAR AND MECHANISTIC ASPECTS OF THE FUNCTIONALIZATION OF POLYOLEFINS WITH ESTER GROUPS

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In previous papers we have reported that polymers of monoalkenes (HDPE<sup>1</sup>, EPR<sup>2</sup>, isotactic and atactic polypropylene<sup>3</sup>) can be functionalized in the melt with unsaturated dicarboxylic acid esters such as diethyl maleate (DEM): in the presence of a peroxide initiator. The structure of the grafted groups was shown<sup>4</sup> to be that of 2-(diethyl succinate) (DES).

Ester groups were also grafted on polyolefin chains through reaction with diazoesters<sup>5</sup>. In this case also the structure of the grafted group was confirmed by NMR<sup>6</sup>.

From the application point of view the former process seems to be more reliable and convenient, but is more complex and more difficult to control.

Indeed several side reactions can occur due to the reaction conditions (high temperature and free radical mechanism) and the quantitative aspects are not well understood. Therefore a detailed study under well defined conditions was considered very useful in order to grant a better reproducibility of the functionalization degree (FD) and put some light on the whole mechanism of the reactions system occurring in this process.

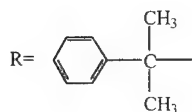
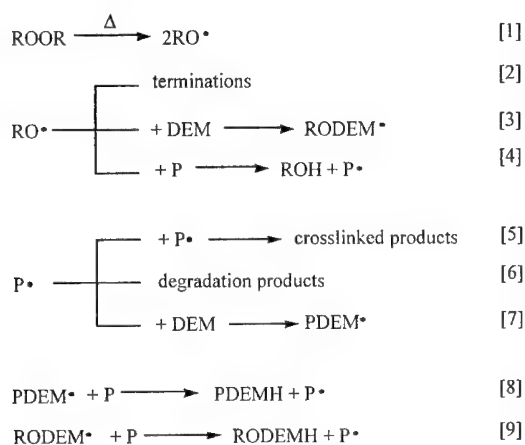
For this purpose several experiments were carried out in the Brabender mixer with 30 min residence time and at constant temperature, 190° C for EPR and 200° C for LLDPE samples, while varying the number of branching in the starting polyolefin, the amount of DEM and of dicumyl peroxide (DCP).

At the end of the reaction, the polymeric product was treated with boiling acetone to remove low molecular products (DEM, DCP residues and oligomers) formed during the reactions as the starting polyolefins were 100% insoluble in that solvent. In general, the acetone insoluble polymer was soluble in heptane and the FDs referred to this fraction were in the range 0.2-2.0% mol of DES groups per 100 moles of monomeric units. When the toluene extraction left a residue, the FD was calculated on the whole acetone insoluble material in order to detect the total amount of grafted groups. The results of the different experiments can be analyzed on the basis of the series of parallel and successive reactions summarized in the scheme.

The contemporary occurrence of the above reactions provide a reasonable explanation of the results obtained and help to select proper conditions for controlling the characteristics and FD of the polyolefin and keep undesired secondary reactions under control. In particular they account for the limited value of FD which can be reached without degrading too much the starting polyolefin and wasting a large excess of DEM.

More detailed quantitative information can be derived from the kinetic investigation, as some of the reactions of the scheme can stop before the end of the reaction time.

Possible process modification to improve its performances as well as extension of the reaction to other polyolefins are discussed.



P= polyolefin macromolecule

**Scheme.** Simplified reaction mechanism of the polyolefin (P) functionalization with diethyl maleate (DEM) and dicumylperoxide (ROOR).

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## ML-9

### MORPHOLOGY AND PROPERTIES OF REACTIVE COMPOUNDED POLYMER BLENDS BASED ON POLYOLEFINE COMPONENTS

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The physical and applicational properties of a multi-component polymer system prepared via a melt mixing process are dependent on the properties of the components, the thermodynamic miscibility of the different polymers, the proportions of the components and the quality of the mixture resulting from the mixing intensity of the melt mixing device and the degree of homogeneity, respectively. In polymer blends based on polyolefinic components with semicrystalline structure, also the crystallization behaviour is playing an important part concerning the property level. Different morphologies of a polymer blend are resulting in dependence on the micro-rheological behaviour of the components during melt mixing. The morphology formation process in heterogeneous polymer blend systems is controlled mainly by the ratio of the viscosities of the components, the ratio of the melt elasticities and the ratio of the acting shear stresses on a melt particle and the interfacial tension. Thus, binary polymer systems with a low viscous dispersed phase and a high viscous matrix phase show a favourable deformation behaviour of the dispersed particles and droplet breaking mechanisms and will form a fine structured phase morphology. In the opposite, if the dispersed phase has the higher viscosity in comparison to the matrix phase, no deformation of the dispersed particles is possible and the blend shows a coarse phase morphology. This is the reason that e.g. even blends from different types of polyethylene can have a very different degree of homogeneity and a pronounced phase morphology. This results in strong differences of the mechanical properties. Different mixing degrees of LDPE/HDPE blends realized by different melt mixing devices are responsible for the dependence of the mechanical properties on the composition of the blend (Fig. 1)

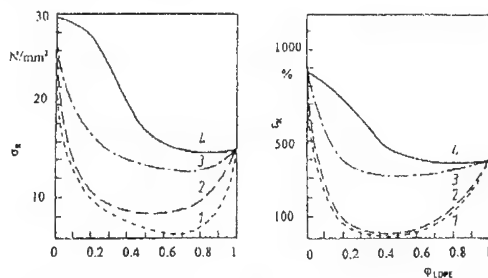


Figure 1: Tensile strength and elongation at break of LDPE/HDPE blends in dependence on composition and mixing intensity of the blend (1: dry blend, 2: ESE-1, 3: ESE-1, 4: DSE)

Because of the thermodynamic immiscibility of the most polymer pairs connected with high interfacial tensions, a further reason exists for the generation of coarse phase morphologies in melt mixing processes. Usually, such phase separated blends show only poor mechanical properties. An improvement of the property level is possible by compatibilization of such heterogeneous polymer systems. Compatibilization means to generate a fine dispersed polymer system with a large inner surface between matrix and dispers phase, and to create a stabilization of the dispersity of the blend to avoid coalescens of the dispersed particles, as well as intensification of phase interactions. Thus, e. g. blends prepared from the immiscible components PP and PS show only poor mechanical properties. Compatibilization of this polymer system by addition of copolymers, reactive agents or surfactants leads to a total change of the phase morphology and an improvement of the phase interactions what is connected with an increase of the mechanical properties (Fig. 2).

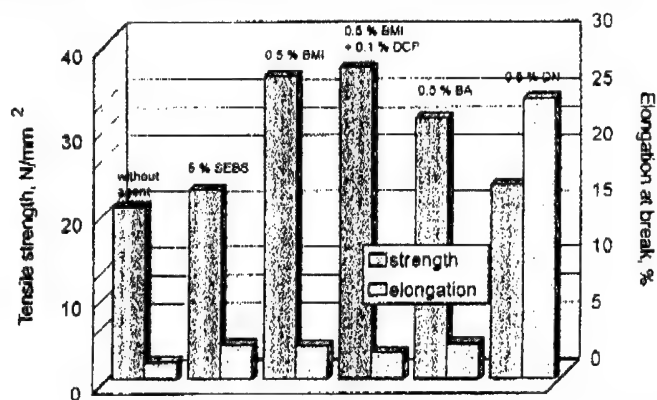


Figure 2: Tensile strength and elongation at break of PP/PS blends modified with different compatibilizers

By reactive compounding processes of polyolefine based blends a very strong change of the phase morphology and the mechanical properties can be realized. An example is the dynamic vulcanization of PP/Rubber blends. Blends of this components with a major proportion of rubber and a special generated co-continuous phase morphology can be transformed into a dynamic vulcanizate with isle-matrix morphology and rubber-similar mechanical properties. Such a change in the morphology is possible by reactive mixing using suitable vulcanizing systems. The very fast increase of the viscosity of the rubber component and the increased shear stresses cause a break of the co-continuous rubber phase in rubber particles included in the PP matrix. This changed morphology guarantees rubber-like mechanical properties at application and thermoplastic processability of the dynamic vulcanizate. The semicrystalline polyolefine matrix is not only responsible for the thermoplastic processability but also for the thermal resistance and stiffness of this type of heterogeneous polymer material.

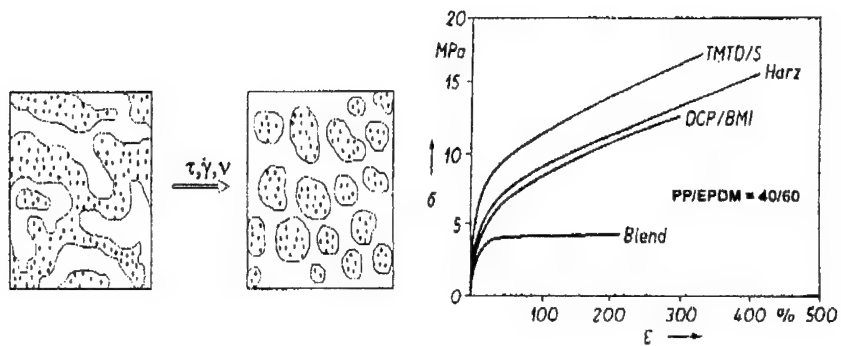


Figure 3: Morphology transformation and stress-strain behaviour of a dynamic vulcanizate based on a PP/EPDM blend

The presented examples show that there exist a strong correlation between the phase morphology and the property level of the polymer blends. Controlled mixing intensily and well-aimed compatibilization are the ways to create polymer blends with optimum properties.



## ML-10

### UNIFORM POLYOLEFIN AND POLYMETHACRYLATE

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Natural polymers such as nucleic acids and proteins are usually uniform with respect to molecular weight, sequence arrangement of constitutional units, stereoregularity and conformation, and the uniformity relates strongly to their biological activity. On the other hand, synthetic polymers are usually nonuniform and thus the characteristics of a polymer sample are always observed as average values. If uniform polymers were available, fundamental understanding of the structures and properties of polymers could be greatly advanced, and thus the preparation of synthetic uniform polymers is an important and challenging subject in the field of polymer science. In 1907 Fischer prepared an oligopeptide, L-G-G-G-L-G-G-G-L-G-G-G-G-G-G-G-G (L = leucine unit, G = glycine unit), which is uniform with respect to molecular weight as well as sequence arrangement of monomer units<sup>1)</sup>. This is the first example of the synthesis of uniform oligomer. The second example was the isolation and characterization of uniform poly(oxymethylene) diacetates with degrees of polymerization (DP) ranging from 1 to 26. The isolation was made by careful solvent fractionations using ether or ethyl acetate at different temperatures. This is a great and challenging work by Staudinger<sup>2-4)</sup> to demonstrate that a polymer comprises a mixture of homologous molecules with high molecular weights.

Later, uniform poly(methylene)s were prepared by a stepwise reaction of oligomers up to a carbon number of 390. These species were then used for a study on the nature of chain folding in lamellar polymer crystals<sup>5,6)</sup>. Lamellar poly(methylene) crystals were prepared from the uniform poly(methylene)s under several conditions, and the number of carbon atoms in the straight stems of the crystals ( $n_{\text{LAM}}$ ) was determined from the longitudinal acoustic mode (LAM) band of low-frequency Raman spectra. The ratio of the number of total carbon atoms in the poly(methylene) ( $n$ ) to  $n_{\text{LAM}}$  was found to be very close to integers which correspond to the number of chain folding. Chain folding was found in all poly(methylene)s with  $n$  of larger than 150. For the case of  $n = 150$ , a lamellar crystal with one folding was obtained. The number of chain folding increased with an increase in  $n$ , and lamellar crystals with a maximum of four folds were obtained in the case of  $n = 390$ . From these observations it was concluded that: (1) chain folding is found in all uniform poly(methylene)s starting with  $\text{C}_{150}\text{H}_{302}$ ; (2) the fold length is always an integral reciprocal of the extended chain length; and (3) the end groups are located at the lamellar surface and the fold itself must be sharp and adjacently reentrant. It should be noted that this conclusion could not be obtained without the uniform poly(methylene)s.

Polymerization or polycondensation of high molecular weight monomers or uniform oligomers with functional groups is one of the more promising means for preparing uniform polymers. In this case, the difference in molecular weight between the components  $i$  and  $(i + 1)$  in the products is not small and the isolation of uniform species can be easily made by chromatography such as GPC. Uniform cyclopolyalkanes were prepared up to a molecular weight of 2805 using metathesis

polymerization of cyclooctene with  $\text{WCl}_6/\text{EtAlCl}_2$  followed by GPC fractionation and subsequent hydrogenation of the uniform polycyclooctene<sup>7,9)</sup>.

The crystallographic form of the cyclopoly(methylene)s changes from triclinic to orthorhombic as the number of carbon atoms increases. The transition from triclinic to orthorhombic occurs gradually between carbon numbers 80 and 160. It is interesting to note that the crystallographic form of poly(methylene) single crystals is orthorhombic and that chain folding in the uniform linear *n*-alkane crystal begins to occur when the number of carbon atoms reaches 150 as described above. The  $^{13}\text{C}$  CP/MAS NMR chemical shift for the methylene carbons in the *trans* zigzag conformation of orthorhombic cyclopoly(methylene)s is 32.8 ppm on average. The value is very similar to that for the poly(methylene) crystal. The cyclopoly(methylene)s showed characteristic peaks between 22 and 27 ppm, ascribable to the methylene carbons in the fold part having *gg'gg* conformation, whose relative peak intensity decreased with an increase in the number of carbon atoms<sup>8)</sup>. The high-field shift from that for the *trans* conformation was explained by the  $\gamma$ -gauche effect. From the comparison with the spectra of the cyclopoly(methylene)s, a peak at 30.7 ppm observed in the spectra of poly(methylene) was ascribed to the fold portion of the poly(methylene). The stem length in the crystal could be estimated from the peak intensities in the spectrum. Thus the uniform cyclopoly(methylene) is also useful for the structural elucidation of poly(methylene) lamellar crystals.

Oxidative polymerization of tetracos-1,23-diyne by Eglinton's method<sup>10)</sup> followed by chromatographic separation and hydrogenation with Pd/C catalyst gave a series of uniform linear alkanes up to  $\text{C}_{38}\text{H}_{770}$ . The same procedure under high dilution conditions provided uniform cycloalkanes up to  $\text{C}_{288}\text{H}_{576}$ <sup>11)</sup>. These linear and cyclic uniform poly(methylene)s were also used for investigating the crystal thickness and folding behavior of lamellar crystals.

In the case of vinyl-type polymers such as polystyrene and polymethacrylate, separation technique with supercritical fluid chromatography (SFC) is highly effective to isolate uniform polymer. Combination of SFC technique with recently developed stereospecific living polymerizations of methyl methacrylate (MMA) enabled us to prepare uniform poly(MMA)s (PMMA)s with high stereoregularities<sup>12,15)</sup>. By this technique stereoregular uniform PMMA's have been isolated up to the 100mer ( $\text{C}_{504}\text{H}_{816}\text{O}_{200}=10070$ ) and characterized by NMR spectroscopy and MALDI-TOF mass spectrometry<sup>13)</sup>. The resulting uniform PMMA's are useful as GPC standards for the calibration of molecular weight and for the direct evaluation of instrumental spreading<sup>12,13)</sup>. The molecular weight dependence of glass transition temperature and melting point was studied using these stereoregular uniform PMMA's<sup>13)</sup>. The mechanism of stereocomplex formation between isotactic and syndiotactic PMMA's were successfully studied by using the uniform polymers<sup>13)</sup>. Thermal degradation behavior of the uniform PMMA's was studied by thermogravimetry and by SFC analysis of the degradation products leading to the estimation of zip length<sup>13,15)</sup>.

Stereospecific living polymerization also enabled preparation of uniform PMMA macromonomer or end-functionalized uniform PMMA by the aid of SFC separation. By using these uniform polymers as building blocks, uniform PMMA architectures such as stereoblock, comb and star polymers, were prepared and characterized<sup>14,15)</sup>. A stereoblock PMMA comprising isotactic (DP = 46) and syndiotactic (DP = 46) chains was found to form intra- and intermolecularly associated stereocomplex in acetone. The phenomenon was studied by GPC and NMR at different sample concentrations and temperatures<sup>15)</sup>.

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CL-1

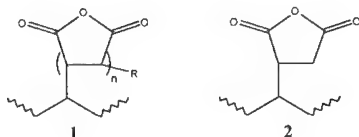
## DEVELOPMENTS IN THE SYNTHESIS OF MODIFIED POLYOLEFINS BY REACTIVE EXTRUSION

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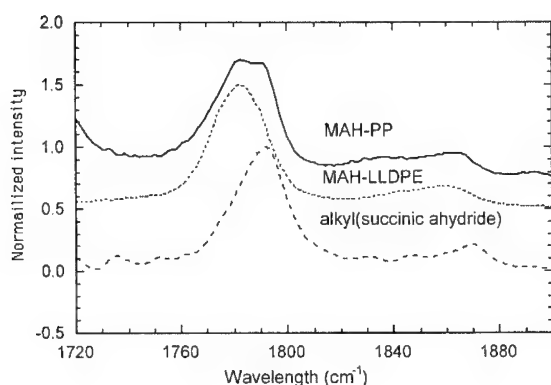
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The advantages of synthesizing polyolefin graft copolymers by reactive extrusion as opposed to alternate technologies are manifold and include (a) no or little use of solvents; (b) simple product isolation; (c) short reaction times; (d) continuous process. Some potential disadvantages or difficulties associated with reactive extrusion are: (a) intimate mixing of reactants and substrates; (b) high reaction temperatures necessary to form the polymer melt; (c) polymer degradation/crosslinking accompanying processing. The potential environmental and economic benefits of the process are such as to justify significant efforts aimed at resolving these problems. Although reactive extrusion and melt phase processing has been in existence for many years, much of the work carried out in this area has been confined to industrial laboratories and little has been published in the open literature. The last few years have seen a turnaround in this situation and a drive to achieve greater understanding of the process. This has brought about a significant increase in the number of publications.

Maleation is one of the most studied polyolefin modification processes yet still attracts much attention.<sup>1-3</sup> We have been investigating this process with a view to gain further understanding of the nature and distribution of grafts and the relationship of these parameters to extrusion conditions.



Although the possibility of oligo(maleic anhydride) grafts (1) has been recognised,<sup>1</sup> until recently it has usually been assumed without proof that maleic anhydride is grafted to polyolefins as single units. Isolated succinic anhydride units (2) can be readily distinguished from the oligomeric grafts (1) by infra-red analysis [oligo(maleic anhydride) absorbs at  $1784\text{ cm}^{-1}$ , succinic anhydride derivatives absorb at  $1792\text{ cm}^{-1}$ ; note maleic anhydride absorbs at  $1784\text{ cm}^{-1}$ ]. This fact was recently reported by De Roover *et al.*<sup>2</sup> who analysed a series of maleic anhydride grafted polypropylenes and found in each instance that a substantial fraction of maleic anhydride units were present as oligo(maleic anhydride). Our analysis of maleic anhydride grafted linear low density polyethylene shows that this proportion is even higher (see, for example, Figure 1) such that all grafts may be oligomeric. This finding is supported by the recent work of Heinen *et al.*<sup>3</sup> who analysed maleic modified polyolefins by NMR.



**Figure 1.** Segments of the infra-red spectra (film) of a maleic anhydride modified polypropylene (MAH-PP), a maleic anhydride modified linear low density polyethylene (MAH-LLDPE), and *n*-dodecyl succinic anhydride.

This finding may provide an explanation as to why maleic modified materials obtained from different commercial sources behave differently even though they have the same nominal composition. The polymers may vary in terms of the length of the oligo(maleic anhydride) grafts, the fraction of succinic anhydride grafts, and/or in the distribution of grafts.

In conducting some aspects of the present study, we have chosen to use metallocene linear low density polyethylenes as substrates. Although, these materials have now been available for some time, very little work has been published thus far on their modification by reactive extrusion. The greater chemical homogeneity and relatively narrow polydispersity of these materials make them ideal substrates for studies aimed at understanding the chemistry of reactive processing. A further benefit is that, depending on density (branching) they have enhanced solubility in a range of organic solvents thus permitting the use of a range of characterization techniques which have been hitherto impractical or difficult to apply.

This talk will detail recent results on the synthesis and characterization of modified polyolefins prepared by melt phase processing in a reactive extruder with a view to elucidating mechanisms for the graft reactions and the nature of the attached functionality. A particular emphasis is placed on grafting reactions which yield reactive functionality to create precursor materials which may be further elaborated into block or graft copolymers.

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## CL-2

### LOW DENSITY ETHYLENE COPOLYMERS WITH ENHANCED CROSSLINKABILITY

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Low density polyethylene (LDPE) is polymerized via a free radical mechanism in a high pressure reactor. The introduction of linear low density polyethylene in the 1970s/80s was expected to drive LDPE out of the market<sup>1</sup>, but this has not been the case. Instead the use of LDPE increases and today LDPE accounts for roughly 1/3 of the total polyethylene market.

LDPE is the preferred material in several applications and has due to its preferable processing characteristics, non polar structure and cleanliness become the favorite in wire and cable applications.

In some applications a modification of the LDPE is needed and this can be accomplished in several ways, i.e. by copolymerizing with a comonomer which contributes with the desired properties<sup>2,3</sup> or by peroxide treatment. A small amount of peroxide, ~0.1 wt-%, is used for the introduction of long chain branches, alteration of the molar mass distribution and to graft monomers onto the polymer backbone. However, if a higher peroxide concentration is used, this results in a crosslinked material<sup>4</sup> where the improved dimension stability at increased temperatures is the most important property change. Crosslinking can also be achieved by radiation and with silanes but at present peroxide crosslinking is the most important technique for commercial crosslinking.

The crosslinkability of polyethylene is to a large extent dependent of the presence of unsaturated structures<sup>5,6</sup>, preferably vinyl groups. In LDPE the content of vinyl groups is low and we found it interesting to see if it was possible to increase the content of vinyl groups by copolymerizing ethylene with  $\alpha,\omega$ -dienes. In the present study two low density ethylene copolymers have been investigated, one with 1,9-decadiene and one with an  $\alpha,\omega$ -divinyl siloxane as comonomer, respectively. In contrast to the catalytic processes used for LLDPE, free radical polymerization is, at least in principle, more flexible as it accepts even polar comonomers. The copolymers have been thoroughly characterized and the peroxide curing characteristics as well as the network formed have been studied. The ethylene-1,9-decadiene copolymer has also been tested on a cable production line. Both copolymers were found to crosslink faster than the reference LDPE and a higher amount of gel was reached. The copolymers also give rise to a more dense network.

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### CL-3

## IMPACT PROPERTIES OF THE POLYMER BLEND OF POLYPROPYLENE AND THERMOPLASTIC ELASTOMER

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### INTRODUCTION

Polymer blends of polypropylene (PP) and various elastomers such as ethylene-propylene random copolymer (EPR), ethylene-propylene-diene terpolymer (EPDM), styrene-butadiene-styrene block copolymer (SBS) etc. have been extensively investigated with a view to the improvement of impact properties [1-3]. High modulus in addition to high impact strength, is also needed for the materials such as the fender of automobile. Here we report on the improvement of impact strength without deteriorating modulus by blending isoprene-styrene block copolymers (ISR) with polypropylene.

### EXPERIMENTAL

The materials used were PP homopolymer (MA3, number-average molecular weight 48,000, weight-average molecular weight 270,000, Japan Polychem Co. Ltd.), ethylene-propylene random copolymer (EPR-07, composition of ethylene/propylene = 73/27 (wt.-%), Kuraray Co. Ltd.) and isoprene-styrene block copolymers (ISR-A, B, C, D, TABLE 1, Kuraray Co. Ltd.). The molten mixing of the materials was carried out at 210°C, the rotary speed was 50 rpm and the mixing time was 5 min. Dumb-bell specimens were molded using a desk injection molding machine (cylinder temperature 210°C, molding temperature 60°C), and the tensile and bending tests, Izod impact test (notched), and dynamic viscoelastic measurements were performed.

TABLE 1.: Compositional data of isoprene-styrene block copolymers

	ISR-A	ISR-B	ISR-C	ISR-D
Styrene content (wt.-%)	30	30	30	60
Specific gravity	0.92	0.92	0.92	0.97
Block type	Di	Tri	Tri	Tri
MFR(230°C, load 2.16 kg)	0.1	70	2.4	0.4

### RESULTS AND DISCUSSIONS

The relation of Izod impact strength and elastomer content for the PP/elastomer blends was shown in FIG.1. The Izod impact strength increased by the addition of elastomer except for ISR-D with high polystyrene content. The maximum impact strength of the PP/ISR-A (100 J/m, ISR-A content 30 wt.-%) was higher than those of PP/ISR-B, ISR-C, and EPR blends (75-85 J/m). In dynamic viscoelastic curves of PP/ISR (70/30) blends, tan  $\delta$  peaks based on glass transition of polypropylene and polyisoprene segments were observed at around 10°C and -50°C, respectively. Although the content of polyisoprene segment of ISR-A, B and C are almost the same, the latter peak height of PP/ISR-A blend was the highest, indicating that the content of amorphous polyisoprene segment of PP/ISR-A is the largest in consistent with the result of Izod impact test. Judging from the relation of flexural modulus and Izod impact strength of the blends with various composition shown in FIG. 2, PP/ISR-A blend is thought to be the promising material having superior balance of impact strength and modulus.

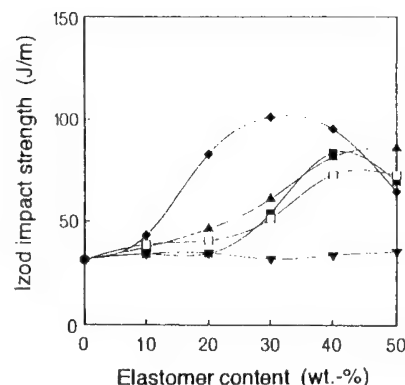


FIG. 1. Relation between Izod impact strength (notched) and elastomer content of the blends

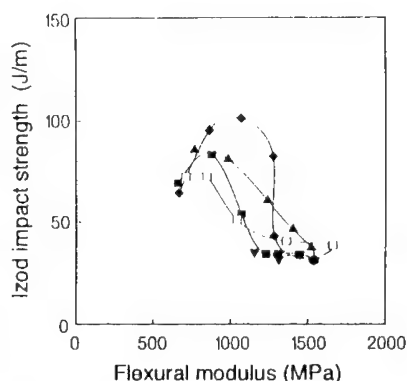


FIG. 2. Relation between flexural modulus and Izod impact strength (notched) of the blends

(●) PP, (◆) PP/ISR-A, (■) PP/ISR-B, (▲) PP/ISR-C, (▼) PP/ISR-D, (□) PP/EPR-07

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## CL-4

### CROSSLINKED LDPE FILLED WITH AN ORGANIC FILLER

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Mechanical properties of low density polyethylene filled with organic fillers have been investigated. Various fillers were used, namely wood particles, aspen fibres, milled grass, recycled paper fibers, starch, and crunched rubber powder. The fillers can be divided in three groups, i.e. isotropic hard particles (wood flour and milled grass), isotropic soft particles (starch), and anisotropic particles (aspen fibres and recycled paper). The three groups behave differently in the LDPE matrix. For unmodified matrix, a drop in tensile strength and slight increase in Young's modulus with increasing filler content was observed for the composites filled with isotropic fillers, while certain increase in tensile strength and substantial rise of modulus values were found for LDPE filled with aspen or paper fibres. A sharp decrease of the elongation at break was found for LDPE filled with hard fillers, either isotropic or anisotropic, while the decrease was much milder if "soft" particles such as starch were used.

Crosslinking of the matrix, initiated by peroxides, leads generally to the increase of polymer - filler interactions resulting in improved adhesion on the phase boundaries. This effect is attributed to a formation of covalent bonds between the polymer macromolecules and the filler surface. Nevertheless, certain differences were observed for different fillers. The values of Young's modulus rise substantially for isotropic "hard" fillers while no change was observed for fibres. The values for PE filled with "soft" filler were even slightly lower compared to uncrosslinked material. Certain increase of elongation at break values was found for "hard" fillers, both isotropic and anisotropic, while no change was found for "soft" particles. The increase in tensile strength was substantial for "hard" anisotropic particles, significant for fibres and marginal for starch particles.

Two modes of crosslinking were investigated. First, the peroxide was mixed in the material at temperature when negligible decomposition occurs and crosslinking was done in a press during compression moulding. Another procedure consisted in a simple reactive processing, when peroxide was decomposed during mixing the filler into the matrix. The materials with different properties resulted from the two procedures.



CL-5

## CRYSTALLINE MODIFICATION OF ISOTACTIC POLYPROPYLENE BY SPECIFIC NUCLEATION

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A technical application of polypropylene, one of the most popular and inexpensive polymers, is limited between others by low impact resistance or low transparency, especially important by packaging utilisation. An important way to improve specific properties of semi crystalline polymers is the addition of small quantities of foreign germination centres, called heterogeneous nucleation. Depending on the structure of the polymer and the nucleation system used, the heterogeneous nucleation may lead to various structural effects.

Due to the increase of the nucleation density a much higher crystallisation temperature, for most of the crystalline polymers, is observed. A homogenous distribution of the nucleation centres in a form of solid crystallisation germs, essentially increases the growth rate of the crystalline domains. In this case the radial growth of the lamellas results in a spherulitical morphology. In isotactic polypropylene the effect of a fast crystallisation is observed due to the addition of nucleating agents like natrium benzoate, derivatives of sorbitols or certain pigments. Another effect usually observed is a modification of the morphology, i.e. creation of a large number of fine spherulites, or even lamellas, followed by significant changes of mechanical, optical and physical properties. On the contrary, the transformation of the crystal monoclinic  $\alpha$  form of polypropylene into the pseudo-hexagonal  $\beta$  form may be achieved by use of particular nucleating agents [1-5]. The well known additive creating the crystallographic  $\beta$  form in the iPP is the linear *trans*-quinacridone, commercially known as Permanent Red or E3B. It was also found that the flow induced stresses in the molten iPP leads frequently to the development of the bi-phasic ( $\alpha$ ,  $\beta$ ) structure in the injection moulded or extruded products.

Recently a new  $\beta$  - form nucleating agent, based on both the pimelic acid and calcium stearate (PACS), was published [6]. This additive, was found to be a very efficient nucleating agent. However, as well for the linear *trans*-quinacridone as for the recently developed PACS - additive, an important dependence of the phase transition on the content and composition of the last nucleating agent was approved.

The nucleation sensitivity was examined for two types of isotactic polypropylene (iPP), distinguished by various molecular mass distribution and various tacticity. The measurements were performed by means of the wide angle X-ray diffraction (WAXS) and the differential scanning calorimetry (DSC). The aim of the

experiments was to clarify how both parameters, the thermal history and the composition of the nucleating system influence the  $\alpha \leftrightarrow \beta$  phase transition of the iPP.

Already for the iPP, nucleated with a linear *trans*-quinacridone, a significant relationship between the concentration of the additive and the  $\beta$ -phase content (k-value according to the Turner-Jones proposition - 4) was detected. A maximum of the k-value, corresponding to the importance of the phase transition, was found for a very low concentration of the  $\beta$  phase nucleating agent, of about  $10^{-4}$  wt. %. A significant lowering (Figure) of the k-value for higher and smaller concentration of the *trans*-quinacridone may be due to the thermal conditions of crystallisation in the presence of a high concentration of the nucleating additive, and to the insufficient  $\beta$  nucleation activity for a low concentration of this specific additive.

A composition of a pimelic acid with a calcium stearate was found to be a very efficient  $\beta$  nucleator, what was confirmed by the WAXS measurements in the transmission mode. The k-value of about 98 % was found for certain compositions of this nucleating system. On the DSC melting curves a characteristic shape corresponding to the endothermic melting of the  $\beta$  phase (at about 145°C), followed by an exothermic crystallisation pick and finally endothermic pick (at about 167°C) representing melting of the  $\alpha$  phase, are well visible (Figure). However, it was also ascertained that the shape of the DSC melting curves as well as the values of the melting temperature depend strongly on the hexagonal  $\beta$  phase content in the iPP, and also on the thermal history of the nucleated samples.

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CL-6

## LOCALIZATION OF DEFORMATION IN SEMICRYSTALLINE POLYMERS

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Several levels of structural hierarchy can be distinguished in semicrystalline polymers starting from the molecular architecture through supermolecular morphology up to macroscopic defects and specimen geometry. Accordingly, deformation processes in a polymeric body under mechanical stress can also be observed at individual structural levels using suitable methods.

In this communication the light scattering and densitometry methods were used to characterize heterogeneous structures of polypropylene-based materials before and after solid-state deformation. On the basis of a theoretical model developed earlier [1,2], spherulites and embedded rubber particles, on one hand, and open voids, on the other, could be distinguished as light scattering elements. It could be shown that the degree of local strain concentration in microregions, as monitored by stress whitening, decreases with increasing drawing temperature. This observation seems to support the notion of stress-induced melting during solid-state drawing at elevated temperature. Moreover, it has practical consequences for optimization of strength and toughness of oriented polymers [3]. The interrelation between local plasticity and macroscopic neck geometry has been described in terms of feedback mechanisms.

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CL-7

## POLYMORPHISM OF ISOTACTIC POLYPROPYLENE IN BLENDS AND COMPOSITES

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The polymorphism of isotactic polypropylene (iPP) is a subject of many works [1-3] but the mechanism of formation of particular forms and transformation from one phase to the other still remains unsolved.

Comparison of all iPP polymorphic structures indicates that the differences between them consist in relatively small changes in the arrangement of helices in the crystal lattice. These observations, in connection with an energetic calculations, led us to a conclusion that one of the reason for the formation of the given form are perturbations in the mobility chains during crystallisation [4]. These perturbations make it difficult for polymer chains to reach the lowest potential energy arrangement, that is to form the  $\alpha$  modification. A acceleration or a retardation in the mobility chains can be caused by introduction to the polymer some specific small molecular weight additives, by mixing the iPP with another polymer or by external forces like pressure or electric field.

According to our hypothesis the formation of the of pseudo-hexagonal  $\beta$  phase in the presence of specific additives, is connected with retardation of the iPP macromolecules mobility caused by interactions between introduced compounds and polymer chains [5].

When the interactions in question were weakened by electric field then a significant decrease of  $\beta$ -iPP was observed [6]. Similar reduction of the activity of the  $\beta$ -nucleants was observed after anisothermal crystallisation under elevated uniaxial pressure (order of  $1.4 \times 10^4$  Pa). This effect differs quantitatively with the additive used [7].

Another interesting problem is the polymorphism of iPP in the blends with thermoplastics or in the composites with natural fibres.

An analysis of the crystalline structure of a blend consisting of amorphous polycarbonate (PC) and semicrystalline iPP has shown that during pressure crystallisation, besides the monoclinic  $\alpha$  phase, the triclinic  $\gamma$  form of iPP occurs. However this  $\gamma$  form was not observed when at the same thermal and pressure conditions only iPP, without the PC, was crystallised. The pressure used in our experiment was much lower than that applied by Sauer and Pae [8].

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A disappearing of obtained  $\gamma$  phase after recrystallisation in non-pressure conditions showed on the a specific role of PC in a formation of triclinic modification [9]. It is interesting that a similar results were noted in the case of the iPP blended with semicrystalline polyamide-6.

In the composites of iPP with natural fibres like flax or hemp the formation of the pseudo-hexagonal  $\beta$  polymorph together with the  $\alpha$  form was noted. A dependence between the amount of this phase and a content of natural fibres in the composite was observed.

*Acknowledgement:*

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## PREPARATION AND PROPERTIES OF CONDUCTING POLYOLEFINS COMPOSITES

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Polyolefins are traditionally used as electrical and thermal insulators. The combination of conventional polymers with conductive polymers or fillers allows to create new polymeric materials with unique electrical properties. Polyolefins can find new applications e. g. as antistatic plastic films or electromagnetic shielding by blending with polypyrrole, polythiophene, polyaniline or other conducting polymers. Also carbon black, graphite or other conducting fillers can be used for this purpose. In such composites the insulating polymer provides good mechanical properties and processability and the conducting polymer or filler provides electrical conductivity. Conductive composites have some advantages compared to bulk metals. Their density is lower compared to that of metals and the processing is similar to that of polymers. In addition, it is possible to vary the conductivity of composites by varying the concentration of fillers.

In this work two kinds of conducting composites were prepared using isotactic polypropylene as a matrix.

The method of chemically oxidative modification of polypropylene particles in suspension by pyrrole was used for preparation of conductive polypropylene/polypyrrole (PP/PPy) composites [1].

Another type of PP/PPy composites was prepared by mixing of pure PP with chemically synthesised PPy at 200 °C, using a Plasti-Corder kneading machine (Brabender).

To investigate the effect of various fillers on electrical properties of composites at the same filler concentration, the polypropylene/carbon black (PP/CB) composites were prepared by mixing pure PP with CB using the kneading machine at 200 °C.

The weight percentage of polypyrrole in the composites was determined by means of elemental analysis. Infrared spectra were recorded using the diffuse reflection technique. The morphology of pure PP and PP/PPy composites was observed using a low voltage scanning electron microscopy. Discharging characteristics of the composites were compared with the behaviour of unmodified materials [2]. Mechanical properties of all types of composites were investigated and dynamic mechanical testing was also carried out.

The influence of the amount of polypyrrole and carbon black in the composites on their electrical conductivity was investigated. The conductivity comparison of PP/PPy and PP/CB composites is shown in Figure 1. The PP/PPy composites were prepared by chemical modification at the same reaction conditions,

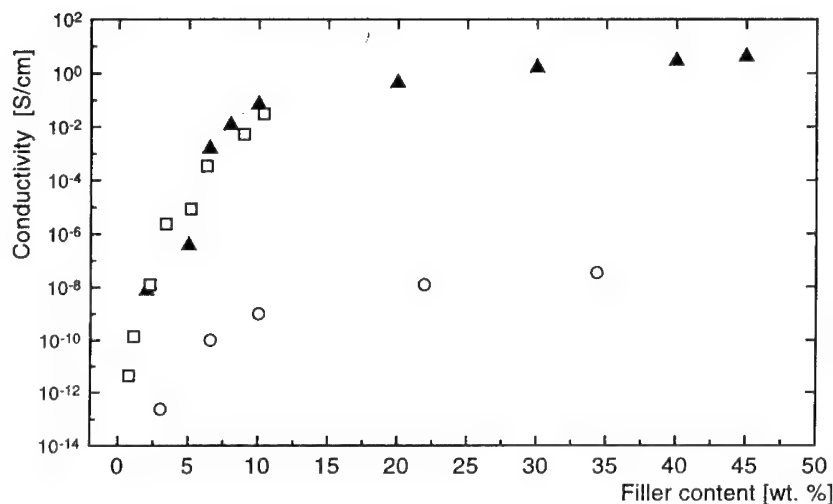


Figure 1. Conductivity dependence of (□) PP/PPy composites prepared by chemical modification, (○) PP/PPy composites prepared by mechanical mixing, and (▲) PP/CB composites on filler content.

while the concentration of pyrrole varied from 1 to 10 wt.%. The polymerization time was 4 h. Bulk conductivity of pure PP was measured to be about  $10^{-16}$  S/cm. Even a very small PPy amount present in composites results in a significant conductivity increase. The increase of the content of PPy from 1.1 wt.% to 8.9 wt.% in PP/PPy composites results in an enormous enhancement in conductivity by seven to eight orders of magnitude. The melt mixed PP/PPy composites show considerably lower conductivity than the composites prepared by the chemical modification method. The difference in conductivity is about 7 orders of magnitude for the same PPy concentration and the conductivity values do not exceed  $10^{-8}$  S/cm, even when PPy content is 34.2 wt.%.

The conductivity of PP/CB composites on CB content showed similar tendency to that of PP/PPy composites prepared by chemical modification. The percolation threshold CB concentration was found between 5 and 8 wt.%.

Electrical conductivity of prepared composites reached values in the range from  $10^{-12}$  to 5 S/cm, depending on the filler content and preparation method.

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CL-9

## PECULIARITIES OF THE PHYSICAL BEHAVIOUR OF HIGH MOLECULAR WEIGHT STABILIZERS IN POLYPROPYLENE

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The efficacy of stabilizers in polymers depends not only on the chemical structure but also on physical factors, including their solubility, diffusion and washing-out by liquids. The increase in molecular weight of the antioxidant reduces its loss due to diffusion from the polymer; on the other hand it gives rise to a decrease on its solubility in the polymer. The dissolution and diffusion of high molecular weight stabilizers require a high energy and great local free volume in the polymer, so these processes should give rise to change in the polymer structure which is facilitated by a high temperature.

In this work, the solubility, diffusion and washing-out of four new sterically hindered amines with molecular weights: 2758, 2286, 1393 and 1364 in PP were studied.

It was shown that the temperature dependencies of the solubility and diffusion coefficient of the stabilizers in PP in Arrhenius coordinates are represented by two broken lines with interruptions near 90-105°C showing a strong difference in the heat of solution and activation energy at high and low temperatures. The solubility of the stabilizers in PP at high temperatures (100-130°C) is time dependent: it passes through a maximum with time and changes with the stabilizer molecular weight in the following order: the higher the molecular weight of the stabilizer the higher its solubility in PP. The diffusion coefficient of the stabilizers in the polymer above 90°C also depends on time.

The studied antioxidants in spite of their high molecular weight leak from the polymer in heptane and in chloroform solutions. There is no simple correlation between the loss of the stabilizers and their molecular weight: the rate of loss of the stabilizer with m.w. 2758 is higher than that of the stabilizer with m.w. 2286. The residual concentration of stabilizers in PP remains after washing-out and this concentration depends on the stabilizer and on its initial concentration in the polymer. The rate of washing-out strongly depends on the solubility of solvent in the polymer.

FTIR spectroscopy measurement of PP films containing stabilizers shows a change in the crystallinity and in the content of regular and irregular conformers in amorphous zone of PP.



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CL-10

**CHEMILUMINESCENCE AS A METHOD OF EVALUATION OF  
OXIDATIVE TRANSFORMATION OF POLYPROPYLENE**

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Accelerated oxidation of polypropylene initiated by various reagents or thermally belongs to common approaches of its further transformation. The processing which follows is, however, effective only when the decay of the molecular mass of the original polymer is not too high and polymer retains the most of its mechanical properties as well as the stability. The control of the oxidation progress may be performed by chemiluminescence tests which provide the information about the length of the remaining induction time.

Oxidation of polypropylene foils initiated thermally was thus measured in oxygen and in air within the temperature interval 100-150 °C and the results of chemiluminescence and mass uptake experiments were compared. It was found that while induction time in air and oxygen is comparable, there exists a significant reduction of the maximum level of chemiluminescence intensity and mass uptake for samples measured in air.

The mechanism of the process is discussed in the framework of monomolecular and bimolecular decomposition of hydroperoxides as the decisive step in the initiation of the polymer oxidation.

# **POLYPROPYLENE DEGRADATION BY THE EFFECT OF ORGANIC PEROXIDES IN SOLID STATE**

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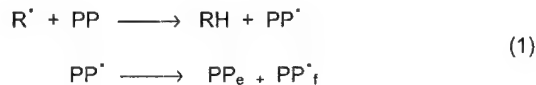
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Peroxide is often used for the initiation of modification reactions on polypropylene [1-3]. These reactions are mainly used for controlled lowering of molecular mass, crosslinking or grafting of polypropylene with other monomers. The mentioned modification reactions are always accompanied with the fragmentation of the polypropylene - PP chain. As has been observed earlier, various types of peroxides have various efficiency in modification reaction and there is also no simple proportional relationship between efficiency of peroxides and the level of polypropylene degradation. From this aspect clarification of the separated effect of initiation radicals on the degradation of polypropylene macromolecules below the melting temperature of PP appears to be interesting.

The efficiency of peroxides on level of degradation of PP at temperatures between 90 and 140 °C i.e. in the range where polypropylene still remains in the powder form has been studied. The following five peroxides were used:

tert. butylperoxy-2-ethylhexanoate - TBPEH, tert. butylperoxyisobutyrate - TBPIB, dialauroyl peroxide - DLP, tert. butyl perbenzoate - TBPB and 1,1-bis(tert. butylperoxy)-3,3,5-trimethylcyclohexane - BTBMC. The level of PP degradation was characterized by flow index (MI) of the polymer melt at 230 °C.

It was found that within the lower concentration region of peroxides applied, fragmentation of PP<sup>\*</sup> macroradicals - an unpaired electron on the backbone - formed by transfer reaction of radicals R<sup>\*</sup> from the peroxide being decomposed, prevails



In fragmentation the polymer chain of PP split into a smaller fragment PP<sub>e</sub> and the end radical PP<sub>f</sub><sup>\*</sup>, with the polymerization degree lower than that of the original macroradical PP<sup>\*</sup>.

Using the equation

$$Mi_d^{0.294} - Mi_o^{0.294} = k [RO - OR]^n \quad (2)$$

where  $Mi_d$  and  $Mi_o$  are flow indexes of the degraded and original polymer melt resp., exponent  $n$  characterizes the mechanism of degradation, was used for determination of relative efficiency of peroxides on PP degradation. The efficiency is characterized by the value of the relative rate constant  $k$  in equation (2).

Peroxide	TBPEH	TBPIB	DLP	TBPB	BTBMC
Relative efficiency of degradation	1	1.7	2.1	26	28

The remarkable increase in the efficiency of TBPB is due to the known fact that decarboxylation of benzoyloxy radical is by about 3 to 5 orders slower than of aliphatic acyloxy radicals.

#### References:

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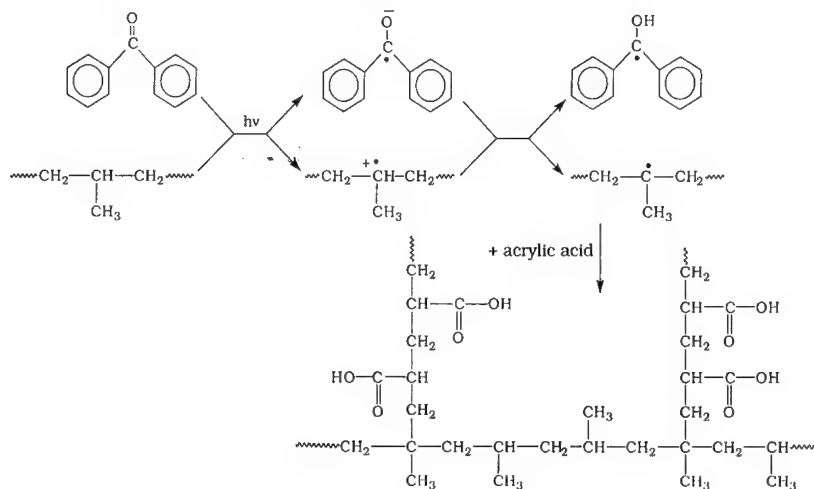
## SURFACE MODIFICATION OF POLYOLEFINS BY PHOTOGRAFTING OF ACRYLIC MONOMERS

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The photoinduced grafting of monomers is one of the most efficient methods to modify rapidly the surface characteristics of organic materials. Depending on the hydrophilicity of the monomer used, the surface energy can be varied in a large range. The UV-curing technology has been successfully applied to poly(vinyl chloride)-based materials, which have thus been made more resistant to organic solvents, abrasion, scratching and weathering. In the case of polyolefins, the process is more difficult to implement because of the presence of less reactive sites on the polymeric chains. The usual grafting method consists in the creation of hydroperoxide groups in the bulk of the polymer by  $\gamma$  irradiation in the presence of air, followed by a thermal treatment to generate the macroradicals which will initiate the grafting reaction of the monomer.

The originality of the photochemical process lies in the fact that the radical sites are produced only at the surface of the polymer sample, where they are to react with the monomer layer. The photoinitiator selected was of the hydrogen-abstraction class (benzophenone, thioxanthone). The excited states formed upon UV exposure of this type of photoinitiator are known to interact with organic compounds by electron transfer, followed by proton transfer:



By reacting with the surrounding monomer, the alkyl radicals formed on the polypropylene chains will initiate the polymerisation and generate polymer chains, grafted at the surface of the substrate. A uniform grafting was achieved by covering the polyolefin film with an aqueous solution of acrylic acid, benzophenone and a surfactant, and exposing the sample to UV radiation for a few seconds. This photochemical treatment was found to modify substantially the surface energy of the polymer: the contact angle of water dropped from 90 to 30 °C, thus making the polyolefin sample hydrophilic and suitable for printing. The grafted polymer was also characterised by ATR infrared spectroscopy. The thickness of the grafted layer was evaluated to be on the order of 2000 nm. Similar results have been obtained with polyethylene, which requires yet a longer UV exposure because secondary hydrogens are more difficult to abstract than tertiary ones.

Another approach which proved equally effective was to coat the organic substrate with a thin film of the photoinitiator, and to cover it with a layer of the neat monomer (hydroxypropyl acrylate). The sample was irradiated for a few seconds, either from the top through the UV transparent monomer layer, or from beneath through the polyolefin support. After solvent development to remove any homopolymer formed, the grafted acrylate polymer was again characterised by drastic changes in the IR spectrum and the wettability (Figure 1).

This grafting process offers the various advantages of photochemical initiation, i.e., ultrafast reaction, low energy consumption, low VOC emission, ambient temperature operations, and on-line processing of large dimension items. Moreover, as the grafting occurs selectively in the illuminated areas, one can produce, after solvent development, high resolution relief images of controlled hydrophilicity.

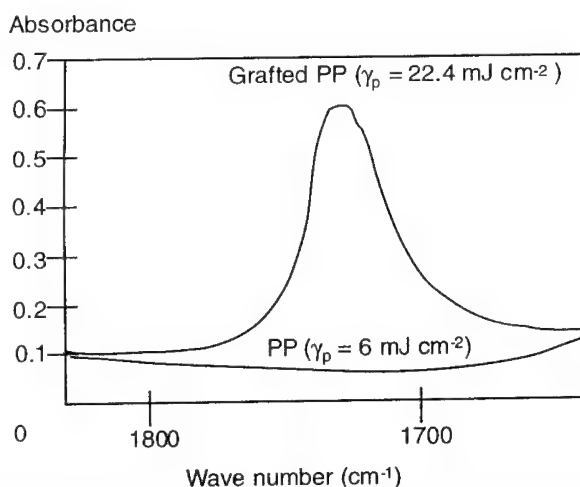


Fig. 1: Infrared spectra of polypropylene and polyacrylate-grafted polypropylene.

# CL-13

## RECYCLING OF POLYOLEFINS, PART I: BLENDS OF TWO POLYMERS

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The most used plastics, specifically in packing and wrapping, are polyolefins(PP, HDPE, LDPE, etc.). These polymers represent about 70% of the plastics used. Because of this high percentage, that is visible in the wastes, and consequently provokes enviromental problems, researchers are studying some ways to solve this serious ecological problem.

The aim of the present paper is to study the feasibility of recycling of polyolefins with some additives as copolymers in order to improves the mechanical properties and increase the useful life pof the blends. In order to develop this goal, several blends were mixed: a) PP with recycled HDPE and b) LDPE with recycled HDPE.

### a) PP/recycled HDPE

The results of the Young'modulus for the PP with recycled HDPE present a slight synergism in the 0-50% range of HDPE although there is not a great dependence of this property with compound. The values of elongation at break reflect the incompatibility of the blends. The resistance to rupture does not show meaningful changes. With respect to the results of impact strength(Table 1), one can affirm that there is a poor interfacial adhesion. This can be attributed to the fact there is not continuity in the interface. The micrographies obtained by TEM show the presence of holes in the interface and the bad dispersion of the minority component in the matrix phase. On the other hand, when the disperse particles are big, these are more effective to begin a process of craking.

HDPE (%)	E (Kg/mm <sup>2</sup> )	$\sigma_B$ (Kg/mm <sup>2</sup> )	$\epsilon_B$ (%)	IS (J/m)	Tf <sub>1</sub> (°C)	Tf <sub>2</sub> (°C)	$\Delta H_f$ (J/g)	X (%)
0	63	3.6	13	7	---	163	150	72
5	68	3.6	10	9	134	156	80	38
10	73	3.4	9	9	130	158	81	38
20	72	3.1	7	7	130	162	83	38
30	71	3.2	7	9	130	159	109	49
40	65	3.1	8	8	131	160	95	41
50	69	2.9	7	7	131	159	90	38
100	65	1.6	560	38	133	----	189	73

Table 1: Values obtained of the Studies Mechanical and Thermal for the PP with recycled HDPE blends.( E: Young's modulus,  $\sigma_B$ : ultimate tensile strength,  $\epsilon_B$ : elongation at break, IS: Impact strength, Tf: fusion temperature,  $\Delta H_f$ : fusion heat, X: crystallinity)

In the thermal studies of the blends (Table 1), the fusion temperatures of the PP as well as HDPE, decrease slightly with the presence of the latter polymers in the blends. This small decrease can be due to the effect of the interplasticizing action caused by a molecule of one of the components that act diluent inside the crystalline of the other component. Another possible cause of this behavior could be the reduction of the spherulitic order. The values of the fusion enthalpy of the blend are below the values of the component. Therefore, the ability of crystallization of a component is hindered by the presence of the other component. The results of the mechanical and thermal properties of the PP with recycled HDPE blends have shown that it is possible to use again the wastes HDPE up to a composition of 30% in weight, decreasing the cost of the raw material as finished product. In order to assess the effect of the addition of compatibilizant agent to the PP/ recycled HDPE blend (70/30), a block copolymer was added to different compositions varying 5 and 20% in weight. The mechanical properties of these blends are analyzed. From these results one can conclude that the optimum composition of this copolymer used is 5%, because the increased of the tenacity and flexibility.

#### b) LDPE/ recycled HDPE

There is an increase of the Young' module related to the increase of the HDPE in the composition. From these results, we can draw to the conclusion that the blends become more rigid in presence of HDPE (Table 2). There is an increase of the elongation at break, up to 40% compositions of recycled polymers. The behavior of these blends, with the exception of the 50% of recycled HDPE, shows a certain degree of interaction in the amorphous phase or compatibility. The reduction can be due to the previous degradation of HDPE, that weakens the tying molecules. Therefore, the material becomes weaker and the rupture occurs before the time expected. The resistance to breaking increases slightly and just in the case of a 50% composition of HDPE, there is sudden decrease.

As the concentration of recycled HDPE increases in the LDPE blends, the resistance to impact decreases. As a result, the compound material loses tenacity since its behavior becomes less ductile. This leads to the following conclusion: the recycled HDPE does not provide the mechanism of energy dissipation.

HDPE (%)	E Kg/mm <sup>2</sup>	$\sigma_B$ Kg/mm <sup>2</sup>	$\epsilon_B$ (%)	IS (J/m)	T <sub>f1</sub> (°C)	T <sub>f2</sub> (°C)	T <sub>f3</sub> (°C)	$\Delta H_f$ (J/g)	Xc (%)
0	15	0.90	83	>200	111	---	---	105	35
10	21	0.94	252	117	108	117	124	126	44
20	26	0.97	325	62	107	120	124	126	45
30	35	1.09	487	32	107	122	125	138	48
40	41	1.13	515	23	108	---	126	146	51
50	35	0.49	9	22	110	---	125	130	46
100	55	1.57	560	38	---	---	133	189	73

Table 2: Values obtained of the Studies Mechanical and Thermal for the LDPE with recycled HDPE blends. (E: Young's modulus,  $\sigma_B$ : ultimate tensile strength,  $\epsilon_B$ : elongation at break, IS: Impact strength, T<sub>f</sub>: fusion temperature,  $\Delta H_f$ : fusion heat, X: crystallinity)

In thermal studies of the blends (Table 2) carried out, a third phase that crystallizes at other temperature was detected. This phase acts by improving the mechanical properties analyzed because it serves as a bond in the interface. Therefore, it is possible to use the recycled HDPE in blends with LDPE, since it is a productive material and reduces the cost of raw material, and, on the other hand, enhances the properties of the finished product.

CL-14

## CHEMICAL MODIFICATIONS OF EVOH AND EAA COPOLYMERS AT THE SOLID STATE (films)

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### Introduction

Alcohols and carboxylic acids groups are among the main products deriving from the ageing of polyolefins. Their identification directly in the polymer matrix is possible by using the powerful Fourier Transform Infra Red spectroscopy however, a best accuracy can be reached if these groups are derivitized into other functional groups as nitrites or acid halides respectively (1). These derivatizations are possible at the solid state (typically on films) by using reactive gases ( $\text{NO}$ ,  $\text{SF}_4$ ,  $\text{NH}_3$ , ...) or the vapour of volatile liquids ( $\text{CH}_3\text{COCl}$ ,  $\text{CH}_3\text{COF}$ ,  $\text{CH}_3\text{OH}$  ...).

Such reactions can be extended to polymers or copolymers containing initially alcohol or acid groups. In the polyolefine family, ethylene-vinyl alcohol copolymers (EVOH) or ethylene acrylic acid copolymers (EAA) are then potential substrates. Both surface and "mass" modifications can be expected according the seeked application (membrane, packaging, printing, coating, ...).

The present communication will concern (i) the conversion of EVOH films containing various amounts of vinyl alcohol into nitrite derivatives (EVONO) and (ii) the conversion of ethylene, propylene, acrylic and methacrylic acids copolymers into ammonium carboxylates ( $\text{COO}^- \text{NH}_4^+$ ) or acid halides ( $\text{COF}$ ,  $\text{COCl}$ ) derivatives. In a second time the reactive acid halides derivatives will be converted into acetate and amide groups by using methanol and ammonia vapour respectively. The evolution of the chemical modification will be followed by FTIR spectroscopy. In the case of EVOH films the evolution of barrier properties will be analysed by gas permeability and surface properties measurements.

### Experimental

EVOH samples were prepared by hydrolysis ( $\text{NaOH}$  0.5 M in methanol, reflux, 48 hrs) of ethylene vinyl acetate copolymers (EVA, Elf-Atochem, thickness 50-100  $\mu\text{m}$ ), 5, 9, 14 and 18 w% of acetate). Acrylic copolymers were obtained from SP2, USA, and pressed into films. Several combinations of ethylene (E), propylene (P), acrylic acid (AA) and methacrylic acid (MA) were studied as copolymers (EAA, PAA, PEAA, PMA). Gases ( $\text{NO}$ ,  $\text{NH}_3$ ,  $\text{SF}_4$ ) and volatile compounds ( $\text{CH}_3\text{COCl}$ ,  $\text{CH}_3\text{COF}$ ,  $\text{CH}_3\text{OH}$ ) were used as received. Chemical treatments have been described in details elsewhere (1), they just consist in putting sample films in contact with gases (PTFE ( $\text{SF}_4$ ) or borosilicate flasks) and left to react few hours to



few days according to the desired conversion. FTIR analysis were made by transmission or reflexion (ATR with Ge or ZnSe crystals) according to the thickness analysed. The use of FTIR microscopy allowed the determination of conversion profiles across polymer films. Permeabilities to N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O were performed on Lyssy instruments. Surface tensions were derived from contact angle measurements on six conventional liquids (H<sub>2</sub>O, HCONH<sub>2</sub>, Hg, CH<sub>2</sub>I<sub>2</sub>, tricresyl phosphate and bromonaphtalene).

## Results

### - EVOH

The NO reaction was characterized both by the decrease of OH IR bands (3400 cm<sup>-1</sup>) and the increase of nitrite bands (1643, 779 cm<sup>-1</sup>). The conversion yield in the film decreased when the initial OH content was increasing however ATR measurements showed that the conversion was almost quantitative in the first 20 µm for all the samples. Significant changes in gas permeabilities and surface tensions were also revealed.

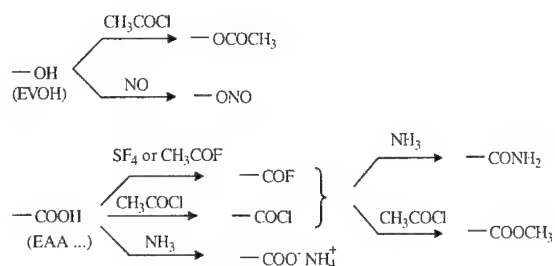
Treatment of EVOH with acetyl chloride vapour allowed to recover rapidly the initial EVA.

### - EAA, PAA, PEAA, PMA

The reaction was characterized both by the decrease of COOH IR bands (1707 cm<sup>-1</sup>) and the increase of derivative bands (COF at 1836, COCl at 1805, COO<sup>-</sup> NH<sub>4</sub><sup>+</sup> at 1555 cm<sup>-1</sup>). In all cases quantitative conversions were obtained.

Subsequent reactions of acid fluoride and acid chloride derivatives with methanol and acetyl chloride vapours were followed at 1736 and 1620/1666 cm<sup>-1</sup> respectively.

Reactions can be summarized as follows :



1. D.J. Carlsson, R. Brousseau, C. Zhang and D.M. Wiles, Chemical Reactions in Polymers, ACS Symp. Ser. 364, 1988, 376.

## CL-15

### **$^{13}\text{C}$ NMR STUDY OF THE GRAFTING OF $^{13}\text{C}$ LABELED MALEIC ANHYDRIDE ONTO PE, PP AND EPM**

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Grafting of maleic anhydride (MA) provides a relatively straightforward and inexpensive route for increasing the polarity and reactivity of polyolefins. The grafted products find widespread application as adhesion promoters or compatibilizers for polymeric blends. Many studies have been published on MA functionalization, but most of them are limited to practical procedures for preparation. The chemical structure of the grafted materials has been the subject of much speculation, but thorough experimental studies are rare. As a result the mechanism of grafting is still a matter of debate.

MA with 99%  $^{13}\text{C}$  in the double bond, (2,3- $^{13}\text{C}_2$ ) MA, was synthesized and grafted on a series of PE, EPM and iPP samples in the melt, using a mini-extruder, and in solution. 1D INADEQUATE  $^{13}\text{C}$  NMR spectroscopy yields high resolution spectra that allow the characterization of the products. A series of low molecular weight succinic anhydride derivatives have been synthesized for assigning  $^{13}\text{C}$  chemical shifts. It is shown that only saturated MA graft structures are formed. In random EPM MA attaches to methylene and methine carbons in the backbone (I and II, resp.). In alternating EPM and in iPP MA attaches solely to methines (II and III, resp.). In EPM and iPP grafts consist of single anhydride units, in HDPE and LDPE short grafted MA di- and trimers are also present. In polyolefins containing sufficient propene sequences, chain scission yields structures in which the anhydride ring is attached to the chain terminus via a fully substituted double bond (IV). All graft structures are rationalized using a simple grafting mechanism.

**INTERMACROMOLECULAR REACTION OF 2-DIETHYLSUCCINATE  
CONTAINING POLYOLEFINS WITH POLY- $\epsilon$ -CAPROLACTAM  
(NYLON 6)**

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The intermolecular reaction between amino end groups of Nylon 6 and diethylsuccinate functionality grafted onto LLDPE and EPR has been investigated in the melt using a Brabender mixer. The reactive blending experiments were carried out at constant 70/30 w/w ratio between the functionalized polyolefin and Nylon 6 at 245°C for 10 minutes at 30 rpm. The recovered polymer was sequentially extracted with formic acid and boiling *n*-heptane<sup>1</sup> (Table 1).

Table 1: Fractionation by solvent extraction of the products obtained by reactive blending of DEM functionalized polyolefins (2DES-g-PO) with Nylon-6 (PA6).

Run	Polyolefin	FD <sup>a</sup>	Formic acid sol. (%w)	Heptane sol. (%w)	FD	Residue (%w)	PO/PA6 <sup>c</sup>
BE01	LLDPE	0.0	26.0	74.0	0.0	0.0	-
BE02	LLDPE	0.7	23.5	57.5	0.6	19.0	73/27
BE03	LLDPE	1.3	25.0	59.0	1.2	16.0	72/28
BE04	LLDPE	1.7	22.0	59.0	1.5	19.0	62/38
BL01	EPR	0.0	19.2	78.9	0.0	1.9	-
BL02	EPR	0.3	16.0	59.3	0.3	23.5	43/57
BL03	EPR	1.9	15.8	54.4	1.5	29.8	52/48
BL04	EPR	0.3 <sup>b</sup>	25.1	65.3	0.1	8.4	45/55

a: FD of the starting polyolefin in moles of grafted 2(diethylsuccinate) groups (DES) per 100 monomeric units of starting mixture.

b: Obtained by mixing 2.6 g of EPR with FD=1.9 and 11.4 g of EPR with FD=0.0.

c: Calculated on the basis of the mass balance.

The characterisation of the two extracted fractions has allowed to demonstrate that the formic acid fraction is constituted of pure PA6 while the *n*-heptane one of pure functionalized polyolefin with the same degree of functionalization of the pristine one. The recover of unreacted PA6 in spite of the large excess of diethylsuccinate functionality ( $-\text{COOC}_2\text{H}_5/-\text{NH}_2 = 4.3 \div 26.3$ ) suggests an indirect evidence for the kinetic control of the grafting/amidation reaction<sup>2,3</sup>. A study is being performed about the influence of additives, catalyst and process conditions on the extent of the intermacromolecular reaction. The formation of polyolefin-nylon (PO-PA6) grafted copolymer has an evident effect on the compatibilization of the two original polymers<sup>4,5</sup>, as revealed by DSC analysis which shows a remarkable decrease of the temperature and the enthalpy of PA6 crystallization. In particular this copolymer shows a SEM micrograph typical of a morphologically homogeneous material suggesting its key role in size reduction of PA6 domains in the blends by improving interface interactions.

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## MODIFICATION OF POLYPROPYLENE WITH ITACONIC ACID DERIVATIVES

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The modification of polymeric materials, specially polyolefins with functional monomers, has been the subject of extensive studies during recent years in order to obtain advanced materials with improved technological properties<sup>1-3</sup>). Several studies that deal with the homo- and copolymerization of olefins with functional monomers and/or modification of preformed polymers have been published.

Polypropylene (PP) has gained an important position among other polymers due to its low cost and its versatile properties for commercial applications. The best known modification of PP is with maleic anhydride<sup>1-6</sup>). It is well known that great scientific and technological efforts have been made to create new technologies for developing special polypropylenes, for instance the use of metallocene catalysts to obtain new homo- and copolymers based on propylene monomer with specific structures and properties. However, the application of PP in different technologically important fields seems to be limited due to its lack of polar functional groups and its inherent incompatibility with other polymers.

Our research group has been working in the past two years studying the incorporation of itaconic acid and its derivatives in PP chains. Results obtained from the functionalization of PP with itaconic acid using xylene and decalin as solvents has been published<sup>7</sup>). The aim of this study was to approximate the reaction conditions to the real conditions of processing of this polymer in an extruder. It was found that polypropylene can be functionalized with itaconic acid in a homogeneous medium for short reaction times with reaction temperatures reaching as high as 190°C and with reproducible percentage of monomer incorporated.

In this communication we present the recent results obtained from the functionalization of PP with itaconic acid derivatives, namely dimethyl itaconate (DMI) and monomethyl itaconate (MMI), in solution by using 2,5-dimethyl-2,5-bis(*tert*-buthylperoxy)hexane (Lupersol 101) or dibenzoyl peroxide (BPO) as initiators and xylene and decalin as solvents. The functionalized PP was characterized by FTIR spectroscopy and melt flow index (MFI). The extent of incorporation of DMI in PP was evaluated from the relation between area of the carbonyl absorption band of grafted PP at 1745 cm<sup>-1</sup> and the absorption band of methyl group from PP at 1167 cm<sup>-1</sup>. This was defined as carbonyl index (Ic) and can be considered as a measure of the extent of grafting. The percentage of grafting (%G) of MMI was determined by a volumetric titration method using 0,05N alcoholic KOH and HCl solutions and thymol blue as indicator.

The following figure and table show some representative results obtained in this study.

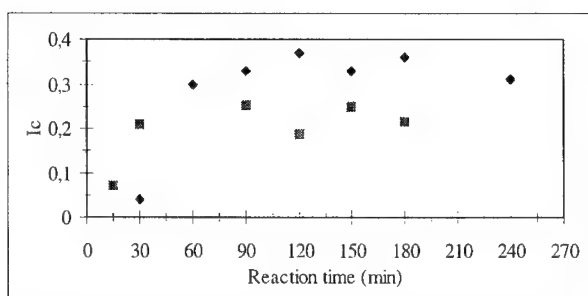


Figure 1. Variation of the extent of DMI incorporated in PP using 10 phr (parts by hundred parts of resin) of DMI and 3.0 phr of Lupersol 101 as initiator in xylene (♦) bp: 135°C and in Decalin (■) bp: 190 °C.

Table 1. Functionalization of PP (MFI = 12,6 g/10 min: 230°C, 2.16 Kg) with MMI.

Solvent	Monomer (phr)	Initiator (phr)	Reaction Time (min)	%G (wt.)	MFI (g/10 min)
Xylene	5	0.5 <sup>a)</sup>	20	0.50	13.6
	5	1.0 <sup>a)</sup>		0.35	32.2
	10	1.0 <sup>a)</sup>		0.34	37.2
	5	1.0 <sup>b)</sup>		1.14	16.6
Decalin	5	0.5 <sup>a)</sup>	20	0.22	26.5
	5	1.0 <sup>a)</sup>		0.40	29.0
	10	1.0 <sup>a)</sup>		0.16	31.2

<sup>a)</sup> Lupersol 101 ; <sup>b)</sup> Dibenzoylperoxide

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# STUDIES ON MORPHOLOGY, RHEOLOGICAL, MECHANICAL AND THERMORELAXATION PROPERTIES OF CHEMICALLY AND RADIATION MODIFIED POLYETHYLENE / ETHYLENE-PROPYLENE-DIENE COPOLYMER BLENDS

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Physical modification of polyolefins by blending with various elastomers is one of the most economic ways to obtain thermoelastoplastics with characteristics both of rubber and plastic, e.g. flexibility, impact strength, etc. Rheologic properties of these materials allows to reshape them by highly productive plastic material processing.

Application of these materials can be considerably enlarged by chemical or high-energy treatment.

Several peculiarities in morphology and structure of these materials as well as changes in rheological, mechanical, adhesive a.o. characteristics in course of investigation of low density polyethylene (LDPE) and ethylene-propylene-diene copolymer (EPDC) blends were observed. Blends were chemically modified by specific crosslinking system (crosslinking occurs basically in elastomer phase, series **A**), and modified by  $\text{Co}^{60}$   $\gamma$ -radiation (crosslinking takes place in both dispersed phases, series **B**).

For example, effective viscosity differs depending on the way of crosslinking of dispersed phases and EPDC content in the blend. Parameters of samples of series **A** and **B** become equal in case of great EPDC content (75 - 95 wt.%) and for absorbed dose of radiation up to 150-200 kGy. Since vulcanizing system affects only the phase of elastomer, viscosity decreases with content of polyethylene phase and finally reaches the level of pure polyethylene viscosity.

Radiation crosslinking affects impact strength at  $-120$  and  $-140$  °C. It is determined that with increase of EPDC content up to 30 % in the blend, impact strength slightly decreases (from 1,3 to 0,8 J). Further increase of EPDC content up to 80 % does not change parameters of impact strength.

There is a definite correlation of wide spectra of characteristics of samples of series **A** and series **B**, containing different amount LDPE and EPDC: density, crystallinity (according to the data of DTA and X-ray diffractometry), micro-hardness, strength-deformation and adhesive properties, testifying priority of radiation modification.

Adhesive properties of mixtures must be mentioned specially. Adhesiveness of series **A** compositions to steel is comparable with a pure LDPE. The peel strength of the adhesive mixtures of series **B** grows with increase of EPDC content and reaches 2-3 kN/m at absorbed doses 50-100 kGy at relatively low contact temperature ( $150-190$  °C) and low pressures (1-2 MPa). This fact is very important to form thermosetting materials (TSM).

It is known that orientation (stretching) of crosslinked polyolefins at high temperature, and subsequent cooling in isometric conditions leads to the material with

thermosetting characteristics (TSM) with an effect of "form memory" at repeated heating. Main TSM characteristics are: thermorelaxation stresses ( $\sigma_{TR}$ ) and residual setting stresses ( $\sigma_{SE}$ ), which remains after TSM cooling under isometric conditions. For series A of low EPDC content  $\sigma_{TR}$  is not considerable in case of pure LDPE (Fig. 1a). With the rise of EPDC content  $\sigma_{TR}$  increases as a result of elastomer crosslinking. However, for series B samples (Fig. 1b) when EPDC content increases,  $\sigma_{TR}$  sufficiently increases but  $\sigma_{SE}$  decreases. It is natural, since  $\sigma_{TR}$  increase at the equal orientation degree is basically determined by effectiveness of crosslinking of LDPE and EPDC amorphous phases which is determined by the absorbed dose. Decrease of  $\sigma_{SE}$  is caused by the drop of crystallinity in blends (from 52 % at LDPE/EPDC ratio 90/10 up to 15 % for the ratio 30/70).

According SEM data, radiation causes levelling of both disperse phases. At the beginning there are specific EPDC phase microgels in the blend (Fig. 2 a). Subsequently by cross-linking of both disperse phases formation of chemical bonds between these phases and fibrilisation of molecular structures is observed (Fig. 2 b). It is testified by isometric heating curves character. There is also noted the dynamic of common  $\sigma_{TR}$  forming of both the phases. There are no separate  $\sigma_{TR}$  maximums of phases.

Consequently it can be stated that LDPE/EPDC blends can be successfully used as elastic thermosetting materials, or could serve as adhesive active TSM interlayer materials.



Fig. 1.  $\sigma_{TR}$  and  $\sigma_{TR}$  for series A samples (a) and series B samples (b) at the heating and cooling in isometric conditions. For series A crosslinking system consisting of captax, sulphur and Zn oxide were used. For series B absorbed dose of  $\gamma$ -radiation was 150 kGy. All of the samples were oriented at the temperature 130 °C. stretching degree – 100 %.

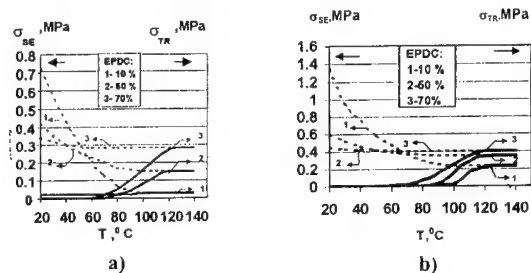


Fig. 2. SEM micrographs of the surface of LDPE/EPD copolymer blend for series A samples (a) and series B samples (b). EPDC content : 50 wt.%. Absorbed dose for series B: 150 kGy.



## IRRADIATION OF POLYETHYLENE IN PRESENCE OF SEVERAL ADDITIVES AS STUDIED BY CHEMILUMINESCENCE

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The interaction of polymeric materials with ionizing radiation is involved in several modern technologies such as radiation processing, production of energy in nuclear plants a.s.o. Oxidation during or subsequent irradiation is an undesired process because it can decrease the service life of the material. Therefore, important efforts are still made to suppress it by means of both syntheses of new materials having inherently high radiation resistance and using of effective additives. Most of the additive molecules found to have an antirad activity can be grouped into two categories according to their mode of action, namely *radical scavengers* and *energy scavengers* [1].

*Energy scavengers* can deactivate to their ground state the excited electronic states of the host polymer. Recent papers refer to effectiveness of some polynuclear aromatic hydrocarbons on stabilisation of polymers against radiation induced oxidation [1,2].

It is also known that pyrolysis of several polymers, such as polyacrylonitrile, polyvinylchloride, cellulose a.s.o. at 500 - 900°C lead to solid residues with condensed povlycyclic structures consisting of graphite like lattices and high spin molecules [3].

The aim of this work was to compare the effectiveness in protection of polyethylene against radiation induced oxidation of a polynuclear aromatic hydrocarbon (pyrene) with those of two phenolic antioxidants, namely Irganox 1010 and Irganox 1222. Another aim was to investigate the effect of the residues obtained by pyrolysis of several polymers such as polyacrylonitrile, polyvinyl chloride, cellulose acetate and methyl cellulose, on the thermal and radiation induced oxidation of polyethylene.

Film or powder samples of both linear low density and low polyethylene containing the above mentioned additives were used.

Chemiluminescence (CL) in both inert and oxidative atmosphere and FT-IR methods were used to characterise the stability of polyethylene samples.

FT-IR data suggest a higher effectiveness of pyrene in comparison with the phenolic antioxidants (see Figure 1). On the other hand, pyrene molecule seems to be more stable to irradiation. Thus, about half of initial pyrene seems to remain unchanged after an exposure of the material to  $\gamma^{60}\text{Co}$  rays at 240 kGy (dose rate 1 kGy/h) in presence of air. Upon the same conditions, about 90% of initial Irganox 1010 seems to be consumed as indicate a comparison of induction oxidation times of initial and irradiated material (see Figure 2).

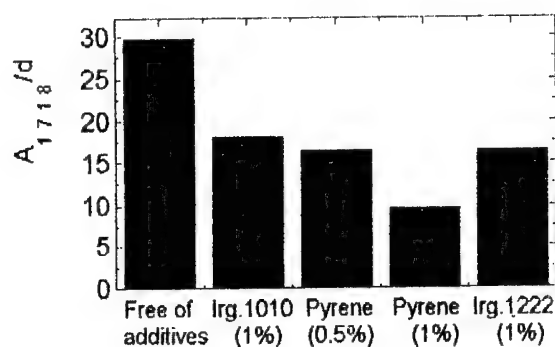


Fig. 1. Carbonyl content of  $\gamma$ -irradiated (240 kGy) LLDPE samples containing various additives

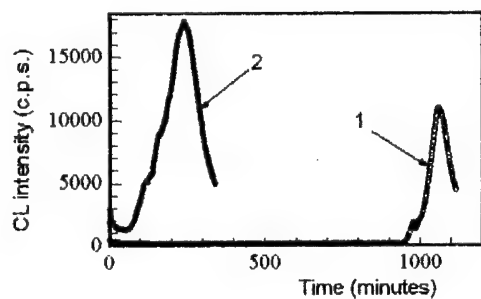


Fig. 2 CL curves from LLDPE containing 1 % of Irganox 1010:  
1 - initial, unirradiated; 2 -  $\gamma$ -irradiated 240 kGy

The stabilising effect of the residues provided by pyrolysis at 850 °C in inert atmosphere of several polymers, such as polyacrylonitrile, polyvinyl chloride and methyl cellulose has been investigated as well.

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CL-20

## MODIFICATION OF PROPYLENE-ETHYLENE COPOLYMERS BY REACTIVE EXTRUSION

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The industrial propylene-ethylene copolymers are a mixture of polypropylene, propylene-ethylene copolymer and polyethylene where this three components may be in different proportions. The molecular weight of these materials is relatively high difficulting the processing due to high melt viscosity and elasticity. One way to improve the procesability is to reduce the molecular weight which may be accomplished, among other methods, by reactive extrusion with the addition of organic peroxides.

The objective of this work is to study the influence of processing conditions and peroxide concentration peroxide on the reactive extrusion of propylene-ethylene copolymers. Two commercial copolymers have being used with a global ethylene concentration of 2.8 (PEC1) and 16.4 wt% (PEC2) respectively. The peroxide used was 2,5-dimethyl-(2,5-diterbutyl) peroxyhexane. The reactive mixtures were prepared impregnating the pellets of the polymers with a dilute solution of peroxide in hexane, and allowing the evaporation of the solvent to give concentrations of 200, 400, and 600 ppm (on weight base) of peroxide. The reaction was carried out in a counter-rotating twin screw extruder. Runs were performed at temperatures of 197, 207 and 217°C and screw rotational speeds of 20, 40 and 60 rpm to give different mass flow rates.

Gel permeation chromatography was used to determine the molecular characteristics of the original copolymers and the modified materials. The molecular weights were calculated by standard calibration with monodisperse PS samples and using Mark-Houwink coefficients for PS and polypropylene in TCB. This technique allows to analyze the relative change in the molecular weights and molecular weight distribution of the modified copolymers. The shear rheological behavior of all the melted polymers was analyzed in capillary and rotational rheometers at different temperatures in the range of usual processing conditions for these polymers. The steady shear viscosity and the viscous and elastic moduli were obtained using steady-state and oscillatory shear flows.

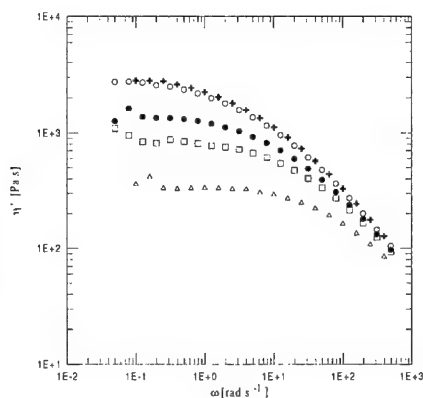
As an example of the obtained results, the annexed Table 1 shows the GPC results obtained for the two copolymers processed at 217°C and 60 rpm modified with different peroxide concentrations. The estimated molecular weight for the original polymers is not noticeably affected during the processing when there is no addition of peroxide. However, all the modified polymers show lower Mw than the parent materials with molecular weights that decrease with the increase in the concentration of the peroxide. This trend in molecular weight was observed at all processing conditions for both polymers.

Figure 1 shows the dynamic viscosity of the set of modified materials corresponding to the first column of Table 1. The modified polymers have lower viscosity than the original copolymer in the frequency range analyzed. The same trend was observed in all the materials and processing conditions with a slight effect of the temperature and residence time.

**Table 1** - Weight- and number-average molecular weights of the copolymers and the modified materials processed at 197°C. The molecular weight were calculated considering the materials pure polypropylene .

Peroxide conc.	PEC1		PEC2	
	Mw	Mn	Mw	Mn
Original	201000	53500	298000	68800
0 ppm	201000	53700	294000	65600
200 ppm	192000	50700	285000	65000
400 ppm	175000	54100	269000	74000
600 ppm	152000	42600	-----	-----

**Figure 1** - Dynamic viscosity data obtained at 187°C for the original PEC1 and the modified materials processed at 217°C. (□) PEC1, (•) processed with no peroxide, (◐) with 200 ppm, (◑) with 400 ppm, and (◒) with 600 ppm



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CL-21

## BLEND OF HMWPE, UHMWPE AND TLCP : PROCESSING AND MORPHOLOGY

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The aim of this work was to define the conditions necessary to mix HMWPE, UHMWPE and TLCP as well as the processability of extrusion.

### experimental procedures

Samples of commercial grade UHMWPE and HMWPE, as well as thermotropic liquid cristal polymer (TLCP) , were obtained from Hoechst.

Blends were prepared with a Brabender plasticorder torque rheometer.

A temperature of 270°C was choosen to process the materials alone or the blends with only one kind of PE, whereas 240°C was used to mix the blends with both UHMWPE and HMWPE. No degradation occurs during processing

Microstructure studies were performed on extruded samples, on microslices for optical investigations and on broken samples for scanning electron microscopy.

### results and discussion

#### - process conditions

Self-heating phenomenon was studied at first. For HMWPE, the temperature exhibits a higher rise than for UHMWPE, although the viscosity of UHMWPE is over that of HMWPE. This peculiar behaviour can be attributed to unmelted UHMWPE particles (1-2) which reduce friction forces between polymer and brabender.

Otherwise, for TLCP, the rise of temperature during mixing is not important due to the low viscosity of this material. This typical feature is used to explain the decrease of PE/TLCP blend self-heating compared to that of PE. In agreement with Paci and al (3), TLCP takes place between PE and metal, reducing friction and then temperature.

Due to the difficult processability of UHMWPE (unmelted particles), we have mixed this one with HMWPE. The evolution of the torque recorded during mixing has led to the optimal rate of UHMWPE : 20%.

The addition of TLCP to previous blend or to PE alone leads to a typical behaviour described for example on figure 1.

The decrease of the torque with the increasing rate of TLCP can be inputed either to the migration of TLCP towards the polymer-metal interphase, or to interfacial slippage between the two polymers (4-5). Another possible explanation may be that, due to the increase in TLCP concentration, the chains within the polymer blend become stiffer and resist less to the shearing force.

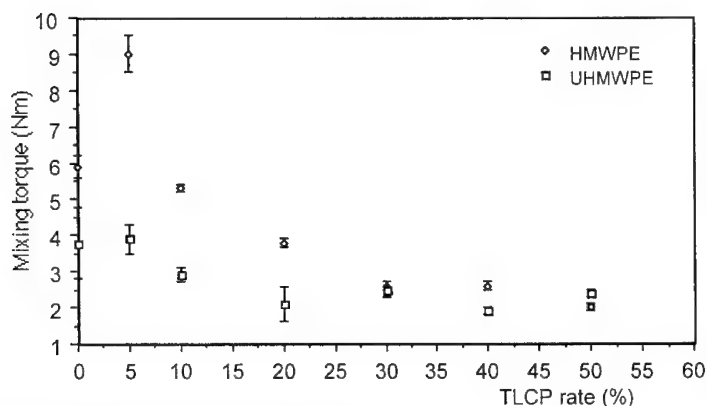


Fig. 1 : mixing torque versus TLCP rate.

At five weight percent of TLCP, the increase in torque could be attributed to the low concentration of LCP, which would be not sufficient to reduce the friction factor in the solids transport zone of the extruder.

#### - Morphology

The optical microscopy studies on pure HMWPE show a crystalline uniform material whereas blend HMWPE-UHMWPE reveals an heterogeneous morphology (unmelted particles of UHMWPE)

The addition of TLCP leads to a second kind segregated phase elongated as fibers along the extrusion direction.

The blends of UHMWPE-HMWPE and TLCP can be mixed without too large hindrances. TLCP decreases torque and forms fibers that perhaps will increase mechanical properties. Extrusion tests have been conducted and sheets obtained in industrial conditions with more over 20 % of PEUHMW.

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# FIBRE-FORMING BLENDS OF POLYPROPYLENE AND BRANCHED POLYETHYLENE

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The aim of the development of bicomponent fibres based on blends of polypropylene-polyethylene is improvement of some application properties like mechanical and thermobonding properties [1 - 3].

In this paper the fibre-forming properties of isotactic polypropylene (PP) and low density polyethylene (LDPE) with various molecular weight were investigated. Considering the theoretical prediction of the polyfibrillar blends formation the fibres from polypropylene-low molecular weight polyethylene were prepared.

## Material used:

Polypropylene (PP) PP TI 902 (Slovnaft a.s.)

MFI = 27 g/10 min

Polyethylene (LDPE) PE SA 200 (Slovnaft, a.s.)

MFI = 200 g/10 min

Processing of polymer blend was significantly improved at higher content of polyethylene despite of its non fibre-forming character.

From the study rheological properties of the PP-LDPE blends follows that viscosity of polyethylene is much more less than the polypropylene and experimentally found values of the blend viscosity show the negative deviation from additive ones. The nonnewtonian behaviour of the melt is more distinct within 20-50 % of PP in the mixture. Prevailing content of PE component reveals a positive influence on flow properties of the melt (Fig. 1).

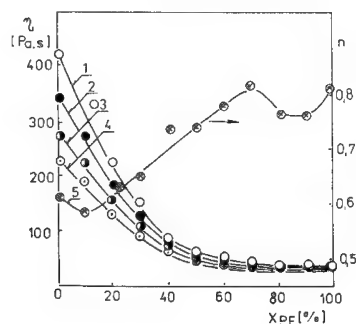


Fig. 1

Dendence of melt dynamic viscosity ( $\eta$ ) and index of newtonial flow  $n$  from Ostwald de Weale's equation on concentration LDPE in the PP-LDPE blend

$\tau$  [kPa] = 1. 8,4; 2. 12,3;  
3. 16,5; 4. 21,7

Polyethylene and polypropylene in mixture shows the individual melting point in whole range. The blends are thermodynamically incompatible. Melting enthalpy of PP is proportionale to its content in blend, melting enthalpy of PE is less because of decrease of its crystallinity.

Tenacity of blended fibers is proportional to the polypropylene content and experimental found values are higher than corresponds to additive rule. The similar character was found also for elongation of the fiber (Fig. 2).

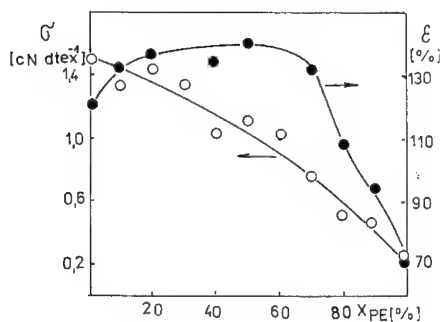


Fig. 2  
Dependence ( $\sigma$ ) of elongation ( $\epsilon$ )  
of blended PP-LDPE fibres on  
concentration LDPE in mixture  
Drawing ratio  $\lambda = 3$

Branched polyethylene significantly increases the relaxation of undrawn blended fibers at 80°C, which disappears at higher drawn ratio. It shows on viscoelastic behavior of low molecular weight polyethylene part in the undrawn fibres. The everage of fibres according to sound measurement (Fig. 3) decreases with polyethylene rate in blend but that was not confirmed by orientation characteristic from optical birefringence.

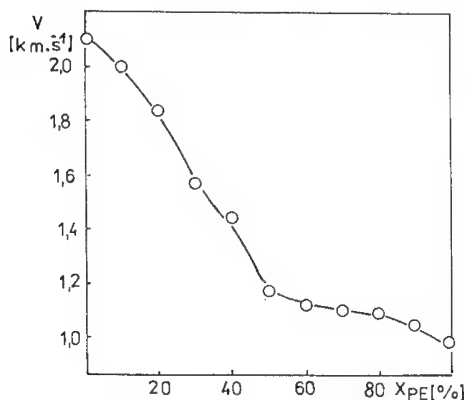


Fig. 3  
Dependence of sound velocity of  
PP-LDPE fibres concentration  
LDPE in blend



From experimental results follows a good technological compatibility of fibre-forming components low molecular weight LDPE and PP at 60-80 % content of "non fibre-forming" LDPE. On the contrary it was found more pronounced in compatibility in the cause of the 60-80 % PP content in the mixture. Very good processing properties were reached at polyfibrillar structure of fibres where dispersed PP phase forms the microfibrils in polyethylene matrix (Fig. 4).

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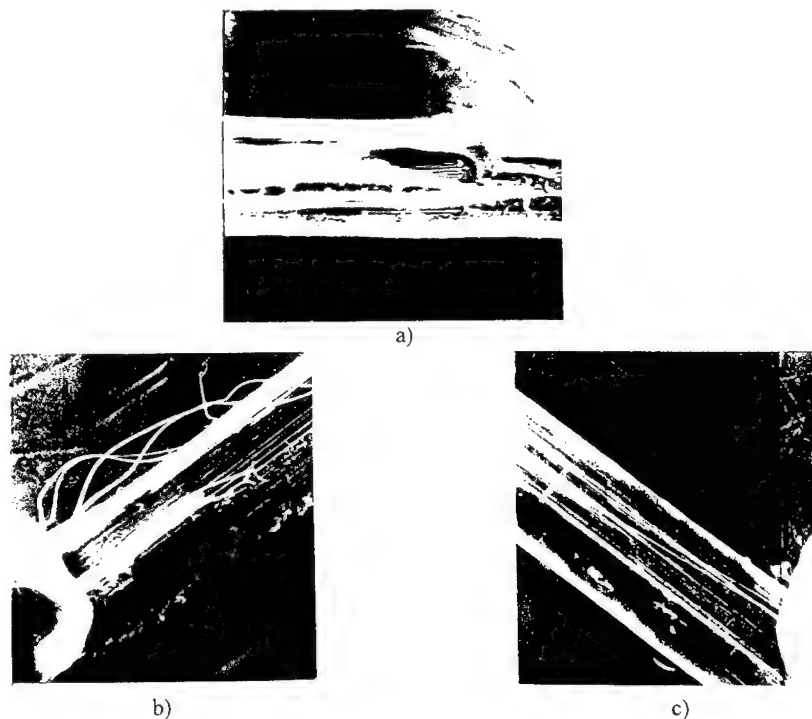


Fig. 4 The polyfibrillar structure of fibres spun from polypropylene - low density polyethylene blend. Drawing ratio  $\lambda = 3$

- a) 100 % LDPE                      b) 80 % PP + 20 % LDPE  
c) 30 % PP + 70 % LDPE

# P-1

## MORPHOLOGY AND ORIENTATION OF PP-STRUCTURAL FOAM MOULDINGS

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The gas-counter pressure process by egression of foamed melt from the core of the moulding is an attractive method for manufacturing of structural foams. Characteristically for this process is the two directional motion and foaming of the gas-containing polymer melt during the mould filling and egression stage [1,2]. From macroscopic point of view the foamed samples have a sandwich-like architecture: cellular core surrounded by a solid integral skin. From microscopic point of view an injected-moulded of polypropylene shows a clear layered structure of skin and core in cross section [3,4]. The aim of the study is to investigate the interaction between the macrostructure and morphology and orientation of polypropylene foam mouldings.

The polymer used was isotactic polypropylene "Buplen" 7523, Bulgarian product, (density  $\rho = 0,901 \text{ g/cm}^3$  and MFI (230/2,16) = 3,5 g/10 min) with 1,0% by wt chemical blowing agent (azodicarbonamide "Genitron"EPA) added. The structural foam samples, center-gated cylindrical plate "disc" (diameter 180 mm, height 11 mm), were prepared on an on-line injection moulding machine KuASY 800/250. The melt temperature  $T_m$  was varied from 200°C to 260°C and the shot weight from maximum shot ("full shot") to minimum shot ("shortest shot") bellow which the production of good quality parts is not impossible. The other processing conditions were constant: mould temperature  $T_f = 20^\circ\text{C}$ , cooling time  $t = 5 \text{ min}$ , gas-counter pressure  $P_g = 1,0 \text{ MPa}$ . Samples were cut from the discs at different distances from the gate (20, 40, 60, 80 mm) parallel and perpendicular to the direction of the flow.

The morphology, the orientation and the processes of nonisothermal melting and crystallization have been studied using polarized optical microscopy, small angle light scattering (SALS), birefringence and differential scanning calorimetry (DSC).

Two layers were observed in the unfoamed skin by the optical microscopy: an outer smectic (amorphous) layer and an inner particular crystalline layer. The thickness of the smectic layer vary from 60 to 100 $\mu\text{m}$  with increasing of the melt temperature from 200 to 240°C. The size of the spherulites increases with the distance from the skin to the foamed core (Table 1). The measured spherulite size in the skin is in accordance with the average spherulite diameter, calculating from  $H_V$ -pattern of SALS. From the  $H_V$ -pattern of crystalline part it can be seen, that the spherulites are not flattened. It was observed the influence of the surrounding birefringence of amorphous areas on the spherulite  $H_V$ -patterns.

Table 1.

	Spherulite size [ $\mu\text{m}$ ]		Melting temperature [K]		Enthalpy of melting [cal/g]	
	skin	core	skin	core	skin	core
200°C	22	35	434,8	431,9	16,01	17,06
240°C	13	37	438,4	4371	16,09	16,71

From DSC curves (Fig.1) was determined the temperature and enthalpy of the phase transitions in the skin and in the core (Table1). The melting curve for the skin has except the main pick, another additional, poorly expressed pick, due to reorganization and following melting of the smectic layer. Because of the imperfection of the spherulites in the foamed core, they melt by the lower temperature compared to the skin.

The orientation in radial ( $\Delta N$ )<sub>r</sub> and tangential ( $\Delta N$ )<sub>t</sub> direction of the flow and perpendicular to the surface ( $\Delta N$ )<sub>p</sub> were studied by birefringence in filling and egression stage. It was found that the decrease of radial orientation with the distance from the gate is more strongly expressed in the outer layer than in the inner layer (Fig. 2).

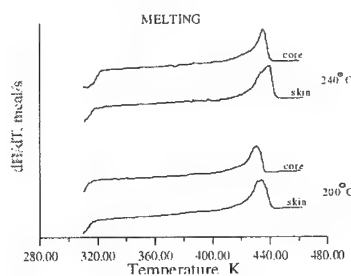


Fig. 1. DSC-curves of melting

The radial orientation decreases near the gate in egression stage due to expansion of gas-containing polymer melt and their motion from the core back to the gate. The tangential orientation is approximately equal on the circumferences concentric towards the gate. The orientation perpendicular to the surface of the moulding decreases from the wall to the centerline (Fig. 3). The largest orientation is observed in the skin layer because of the high shear stresses. In the foamed core which cools slowly the macromolecules have sufficient time to relax and the orientation is low. It was found that the orientation in outer layers decreases with the increase of the temperature of gas-containing polymer melt due to the decrease in melt viscosity.

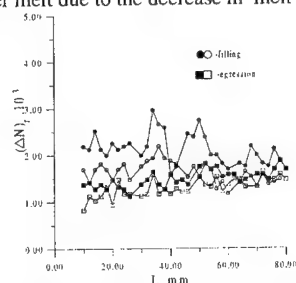


Fig.2. Birefringence vs the distance from the gate in different layers (● -0.3 mm □ -1.4 mm from the surface ).

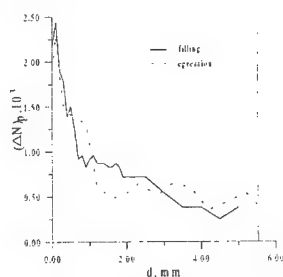


Fig.3. Birefringence vs the distance from the surface

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## P-2

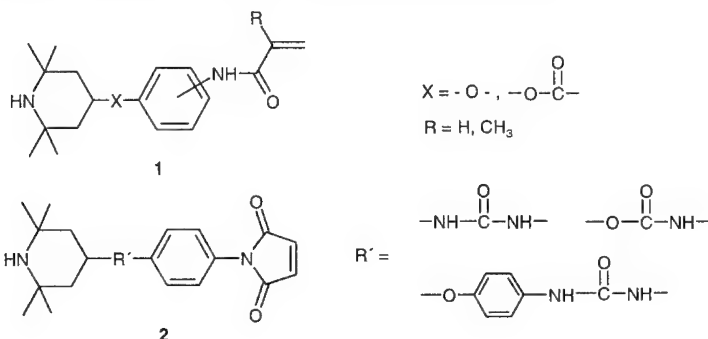
### SYNTHESIS AND CHARACTERIZATION OF NEW HINDERED AMINE LIGHT STABILIZERS (HALS)

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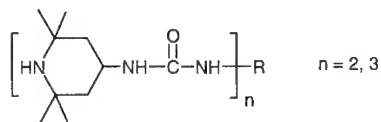
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Getreidemarkt 9, A-1060 Vienna, Austria

The outstanding performance of photostabilizers based on 2,2,6,6-tetramethylpiperidine (HALS) has initiated much work to find ways to reduce the volatility and extractability of HALS from polymeric substrates. In principle, this can be achieved by increasing the molecular weight of the stabilizer or by covalent incorporation into the polymer backbone.

Stabilizers containing polymerizable groups were synthesized by reaction of HALS derivatives with (meth)acrylic acid chloride (1) and 1-(4-isocyanato)-1-H-pyrrole-2,5-dione (2).



In addition stabilizers with increased molecular weight were obtained by reaction of 2,2,6,6-tetramethyl-4-amino-piperidine with several commercially available di- and triisocyanates.



The new stabilizers were characterized by NMR and DSC and the effects in the photostabilization of polypropylene films were investigated.

## THE FORMATION OF THE SOLID SOLUTION BETWEEN REACTIVE BURNING RETARDANTS AND POLYMERS

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A possibility of the formation of homogeneous melt between polymers and low-molecular substance is considered in the present work, since the rate of reactions under such conditions is higher than in heterogeneous ones.

Interesting data are obtained while conducting high temperature x-ray studies of the systems : polymer - low-molecular substance (LMS) and building the diagrams of state. Thus, high-molecular diffractograms of the mixture of polyethylene (PE) and monoammonium phosphate (MAPH) show that at  $T = 136^{\circ}\text{C}$  PE melts and the further increase of temperature ( to the MAPH melting at  $T = 190^{\circ}\text{C}$ ) doesn't change an overall intensity of crystalline MAPH blends. These data indicates that there is no interaction of the components on the level of crystalline structure in the system PE-MAPH. Confirmation is microphotos of the PE - MAPH mixture at different temperature.

Thus, in the system PP-MAPH a solid solution of introduction of MAPH was determined in the PP matrix. The mixture of PP-MAPH heated to  $180^{\circ}\text{C}$  yields a diffractogram with a considerable decrease in the intensity of MAPH, and the absence of PP hand indicates its melting. A diffractogram of the cooled mixture possesses a considerably lowered overall intensity than that of the initial mixture, which indicates the formation of a solid solution.

The formation of solid solutions between a polymer and LMS changes the structure and properties of the composition. For such systems it is necessary to take into account a polymer structure of one of the components. Thus, the effect of a polymer matrix is determined while studying the processes of polyolephines

combustion. Determination of oxygen indices of the compositions on the basis of PE and PP, filled with different amount of the filler ( PER : DAPH : Melamine = 2 : 2 : 1), allows to establish that with small concentrations of the filler combustibility of a polymer slightly decreases, and the formation of foamed coke effects the burning of PE to a lesser degree than that of PP.

Rate determination data of foam-formation according to which the high and rate of foam formation is considerably higher for PP than for PE are in accordance with combustibility (an increase of filler to 40 % oxygen indices state up 28 % for PE and 48 % for PP ; and the rate of foam-formation -  $5.8 \cdot 10^{-2}$  mm/s for PE and  $19.0 \cdot 10^{-2}$  mm/s for PP ). The presence of one and same filler in different polymers (PE, PP), though similar by their physicochemical characteristics maybe can be explained by the formation of solid solution between PP and the filler components. Homogeneity of the melt in case of PP contributes to faster reaction of interaction between the components of the foamed filler, which increases composition resistance against fire. In case of composition on the basis of PE heterogeneity of the system deteriorates the combustibility parameters.

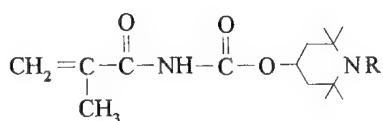
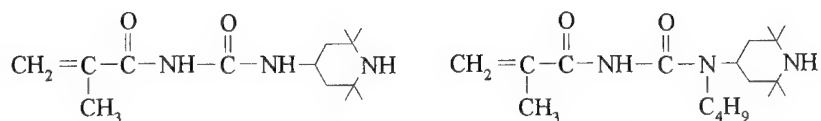
# SYNTHESIS AND CHARACTERIZATION OF NEW MONOMERS AND POLYMERS CONTAINING HINDERED PIPERIDINE GROUPS

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2,2,6,6-tetramethyl and 1,2,2,6,6-pentamethyl piperidine derivatives (HALS) are very effective light- and thermostabilizers for polymers. For many polymer applications, the use of stabilizers with low volatility and low extraction is desired and therefore of high interest.

In this context, we synthesized new methacryloyl ureas (I, II) and methacryloyl urethanes (III, IV) containing a hindered piperidine group. The monomers (I-IV) were prepared by a simple addition reaction of 4-amino- and 4-hydroxypiperidine derivatives on methacryloyl isocyanate.



III-IV (R=H, CH<sub>3</sub>)

The monomers I-IV were polymerized, and copolymerized with styrene by free radical initiation. The structures of these new monomers and their polymers were characterized by IR and NMR spectroscopy and by GPC and MALDI-TOF-MS. Some physical data of these compounds were also given.

# **EFFECT OF STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMER ON THE KINETIC OF THERMOOXIDATIVE DEGRADATION OF HIGH-IMPACT POLYSTYRENE**

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The stability of polyolefins and their blends is very important for their practical use under high temperatures. The thermooxidative stability of high impact polystyrene (PS-HI) and blends of PS-HI and styrene-butadiene-styrene copolymer, (SBS) were investigated. Effect of SBS block copolymer on the intensity of the thermooxidative degradation of HIPS can be followed through kinetic parameters. In HIPS and HIPS/SBS blends, soft, polybutadiene phase (PB), and hard, polystyrene phase (PS) have a different sensibility on thermal degradation. The investigation were done by isothermal DSC analysis. The kinetic parameters of the thermooxidative degradative process: the reaction rate constants, the reaction orders, and the activation energies have been determined. The total area under the exothermic curve was used to calculate the isothermal heat of degradation. On the base of the heat of the thermooxidative degradation of investigated system, the conversion ( $\alpha$ ) and the rate of the thermooxidative degradation ( $d\alpha/dt$ ) have been obtained. The experimental data have been tested with kinetic model for autocatalytic reactions  $d\alpha/dt = k \alpha^m (1 - \alpha)^n$ . The activation energy has been determined by Arrhenius equation.

On the base of the calculated kinetic parameters, the thermooxidative stability of the investigated system in function of amount of polystyrene, has been obtained.

The experimental data have a good agreement with the autocatalytic model.



## DEGRADATION VELOCITY OF NATURAL RUBBER FILMS

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Successful substitution of accelerator, zinc diethyldithiocarbamate (ZDEC) in sulfur cured natural rubber latex films with the combination of two other accelerators, zinc mercaptobenzothiazole (ZMBT) and diphenylguanidine (DPG) was investigated by following the degradation velocity of the monitoring samples. Commonly used ZDEC in latex compounds produces secondary amines which may react with present NO<sub>2</sub> and give N-nitrosoamines which are recognized as cancerous substances.

Investigations of photooxidation and thermooxidation on fully formulated natural rubber latex films, including protective agent, were carried out. Degradation of latex films were followed by IR spectroscopy, measuring the increase of absorbance of hydroxyl and carbonyl groups with time. Physical and mechanical properties were also determined by stress-strain measurement.

According to the results, thermodegradation of latex films is not intensive as photodegradation processes, specially at early stages of the degradation. Parallel with thermooxidation of latex films, additional processes such as crosslinking can be observed. At the onset of thermooxidation usually small addition crosslinking effect may be noticed, arising from polysulphide links rearrangement, and this contributes to an increase of specimens tensile strength.

All obtained results show that mentioned accelerators substitution is a reasonable approach to environmental issues in production of natural rubber latex goods and commodity, as well as technical parts.

**METHACRYLIC ACID AND 2-(3-PHENYL-3-METHYLCYCLOBUTYL)-  
2-HYDROXYETHYL METHACRYLATE: COPOLYMERIZATION,  
CHARACTERIZATION, AND THERMAL ANALYSIS MEASUREMENTS**

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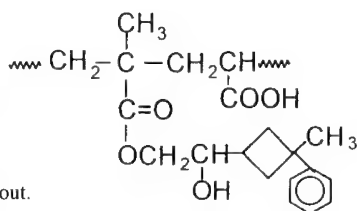
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The homopolymerization of 2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate

[PCHEMA] has been reported by Coşkun et al [1].

But, copolymerization studies have been not carried out.



The free-radical polymerization of methacrylic acid and PCHEMA was carried out at 60 °C in the presence of benzoyl peroxide using 1,4-dioxane as the solvent. The structure of copolymer was characterized by Fourier-transform infra-red,  $^{13}\text{C}$  and  $^1\text{H}$ -NMR techniques. Furthermore, the thermal data of copolymer were obtained using a Shimadzu DSC-50 instrument and TGA-50 thermobalance. Solubility parameters of the polymer was estimated from the solubility test using 1,4-dioxane as solvent and, n-hexane and ethylalcohol as co-nonsolvents. Density measurement of the copolymer was performed with a pycnometer.

**Reference**

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**SPECTRAL PROPERTIES OF COUMARIN DERIVATIVES  
SUBSTITUTED IN POSITION 3. EFFECT OF POLYMER MATRIX***M. KAHOLEK AND P. HRDLOVIČ*

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Spectral properties of coumarin (2H-1-benzopyran-2-one) derivatives substituted in position 3 with bulky substituents like phenyl-, phenylthio-, and benzylthio were investigated in solvents of various viscosity and in polymer matrices. In order to evaluate the effect of heavy atom some derivatives were substituted by bromine in position 6,8. Absorption spectra exhibit broad band with maximum at 340 nm and  $\log \epsilon$  about 4 which is not influenced by medium. Derivatives of coumarin in solvents with low viscosity exhibit broad band fluorescence of low quantum yield 0.005 and lifetime shorter than 0.1 ns. In solvents of higher viscosity and in polymer films, the quantum yields are higher by 0.05 - 0.2 and lifetime by 2 ns, approximately. Based on spectral data, the rate constant of radiationless deactivation  $k_{nr}$  is  $10^{11} \text{ s}^{-1}$  in solution and  $4 \times 10^8 \text{ s}^{-1}$  in polymer matrix, respectively. The activation energy of radiationless process in 3-phenylcoumarin is about  $34 \text{ kJ} \cdot \text{mol}^{-1}$  in glycerol, at the same time the activation energy of viscosity change of glycerol is  $72 \text{ kJ} \cdot \text{mol}^{-1}$ . This comparison indicates that the torsional rotation of the substituent in position 3 is influenced by the friction viscosity of the medium partially.

**Keywords:** fluorescence, coumarin, substituents in position 3, solvent effect, polymer matrix, radiationless process, activation energy.

## MORPHOLOGY OF POLYETHYLENE FOAMED CROSSLINKED SPECIMENS MADE BY HOT MOULD INJECTION MOULDING

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Hot mould injection moulding is a technique for producing foamed thermoplastic low density specimens. Fixation of the specimen macrostructure and shortening of the production cycle can be achieved by crosslinking of the polymer. The crosslinking results in a change of its molecular characteristics and hence the properties of the product. Therefore, the aim of the investigation is to found out the effects of the crosslinking processes on the morphology of polyethylene foamed specimens made by hot mould injection moulding.

A combination of PELD, dicumilperoxide (DCP) and azodicarbonamide (ACA) was used. It provides carrying out of five processes: polymer plasticizing in the plasticizing cylinder at temperature 100-130°C; DCP decomposition, crosslinking of PELD, ACA decomposition and foaming of the blend in the mould. The three components were mixed and granulated in an extruder-granulator at temperature 100-120°C. Mass concentrations in percentage of DCP and ACA in resultant blends are respectively: DCP - 0.08, 0.24, 0.32, 0.40, 0.60; ACA - 5, 10, 15. Test specimens were produced by injection moulding in hot mould which temperature  $T_m$  was 180, 200, 220°C. The degree of crosslinking was calculated by equilibrium strain  $\epsilon_r$  determined at temperature 140°C and pressure stress  $\sigma_p = 0.045$  MPa according formula:

$$N = \sigma_p (100 - \epsilon_r)^2 / \epsilon_r (200 - \epsilon_r) kT,$$

where  $N$  is number of network segment per  $m^3$ ,  $k$  is Boltzman constant,  $T$  is temperature. The same parameter was evaluated by melt flow index ( $MFII/190^\circ C/21.2, 49, 75.5, 134, 212$  N). The degree of crystallinity is determined by DSC-kinetics of a nonisothermal melting and crystallization. The morphology is investigated by a polarizal microscope MIN 8.

It is established that a part of polymer crystallizes as spherulites. The spherulites can observed with crossed polaroids. The samples on the whole are not oriented. There exists only a local orientation around the edge of the bubbles which is proving by the observed bright regions (Fig.1). The number of the spherulites decreases with the increase of crosslinking degree (Fig. 1). This is in conformity with the degree of crystallinity which decreases with the increase of the crosslinking degree, too.



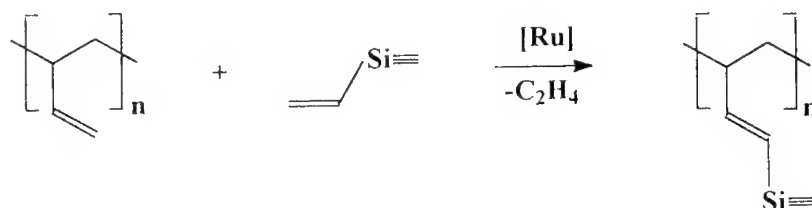
Fig.1. Polarized light micrographs of microtome cuts of specimen at ACA=5% and DCP: a-0.40%; b-0.60%.

# **RUTHENIUM-CATALYZED FUNCTIONALIZATION VS. DEGRADATION OF 1,4-POLYBUTADIENE WITH VINYLSILANES**

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Wagener *et al.* have reported the ADMET depolymerization of 1,4-polybutadiene with silicon-containing alkenes (mainly allylsilanes) using well-defined Mo and W Schrock catalysts [1,2]. In addition, they found that vinylsilanes are not active in this reaction. However, recently, our group demonstrated that ruthenium complexes effectively promote functionalization of 1,2-polybutadiene with vinylsilanes [3]. The overall reaction has been given in the scheme below.



A reasonable step is the extension of this reaction to 1,4-polybutadiene. Following comparable procedures, we observed, in addition to partial functionalization, considerable metathetical degradation of the polymer.

This contribution presents both the catalytic, synthetic and the analytical data of ruthenium-catalyzed functionalization and degradation of 1,4-polybutadiene with vinylsilanes.

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2. J.C.Marmo and K.B.Wagener, *Macromolecules*, 28, 2602 (1995).
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# UNSATURATED 2-OXAZOLINE MODIFICATION OF POLYETHYLENE CONTAINING CARBOXYLIC GROUPS

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The modification of nonpolar polyolefins is still the subject of many research laboratories. The following methods have been used for the initiation of the modification of polyolefins [1]: chemical initiation, photochemical initiation, and high energy radiation induced initiation.

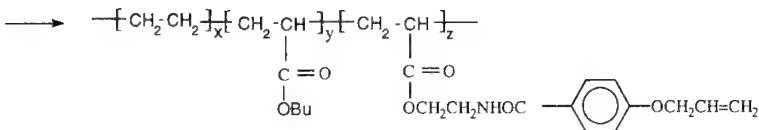
The chemical initiation can include direct reaction of a reactive agent with a polymer at elevated temperature [2], the formation of polymer radicals by the decomposition of peroxides followed by their's reaction with a modifier [2], or a reaction of a functional polymer with a modifier [3].

For the photochemical and high energy initiation is typical direct generation of polymer free radicals (high energy initiation) or polymer free radicals are generated by a chain transfer from the molecule of a photosensitizer to a polymer [4].

Polyolefin modification has found a special application also in polymer stabilization [5] and carboxylation of polyolefins [6]. Interesting is also the modification of polypropylene with carboxylic end group under the formation of a reactive 2-oxazoline structure [7]. In such a way prepared 2-oxazoline terminated oligopropene was used for further modification of poly(ethylene-co-acrylic acid).

The aim of this contribution was chemical functionalization of polyethylene containing carboxylic groups with an 2-oxazoline containing unsaturated group, using the well known nucleophilic reaction between carboxylic group and 2-oxazoline ring [8].

The terpolymer poly(ethylene-co-butyl acrylate-co-acrylic acid) was treated with the modifier 2-(4-allyloxyphenyl)-2-oxazoline in melt and in a solution. The product of such a modification is polyethylene terpolymer containing thermally stable unsaturated allyloxy units in the side chains.



terpolymer was supported by  $^{13}\text{C}$  NMR spectroscopy.

polyolefins.

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## BROMINATION OF POLYOLEFINS

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The reasons for the chemical modification of synthetic polymers include [1]:

1. Changing the physical and/or chemical properties
2. Preparing polymer-supported reagents
3. Controlled release drugs and pesticides
4. Mechanistic studies.

Although most of polymers can be modified, the most known is the modification of chloromethylated polystyrene or its beads where numerous of reactions have been done [2]. Among of commodity polymers, polyolefins can be modified with the aim to obtain new physical properties for improvement of miscibility with other polymers [1,3]. Especially for polyolefins is important also improvement of thermo- and/or photooxidative stability of polymers [4] by a modification with various functional stabilizers. However, for the polyolefins use as polymer supports for reagents and/or for controlled release drugs and pesticides such a modification is necessary that will provide a path for bonding these active molecules to the polymer support. One of these methods is halogenation of polyolefins. Among of halogenation methods, chlorination is the prevailing procedure. On the other hand, chloro groups are not as good leaving groups as bromo groups in nucleophilic substitution reactions. Surprisingly, only few papers have been reported on the bromination of polyolefins [5,6].

In this contribution we report our results on the bromination of atactic polypropylene (aPP), polypropylene oil, and polyethylene (PE) in a solution initiated by heat and by visible light.

Thermally initiated reaction (80 °C) of aPP in dark at the molar ratio aPP:Br=1:2 provided a tacky material with the bromine content 13.5 % after 40 minutes. On the other hand, when the same reaction was performed under the direct action of sunlight, off-white powders were obtained with the bromine content 67.5 % after 110 minutes, and 70.3 % after 200 minutes. Therefore, the initiation with a 60W lamp from 10 cm distance from the aPP solution was applied for better characterization of the modification conditions. In this experimental arrangement, the bromine content 18.5 % was obtained in 5 minutes, and 70.0 % in 130 minutes. In the course of the reaction the molecular weight raised from 2500 dalton for non-treated sample to 7680 dalton for the polymer with the bromine content of 70.0 %. The same reaction conditions, at the molar ratio aPP:Br=1:1, provided yellowish polymer powder with the bromine content 46.0 % during the reaction time of 30 minutes.

Thermally initiated bromination of high pressure polyethylene (HPPE) and linear low density polyethylene (LLDPE) at 80 °C provided practically the same bromine content after 360 minutes (17.5 % for HPPE and 18 % for LLDPE). However, the visible light initiated



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bromination provides for HPPE at the same reaction time the bromine content as high as 57 %.

The bromination represents an interesting and flexible way for the modification of polyolefins. This method enables the preparation of the samples with different bromine content. These polymers can be used for further modification of the preformed polymers, and for the preparation of polymer-supported reagents.

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# FUNCTIONALIZATION OF POLYOLEFINES VIA THERMAL DECOMPOSITION OF AZIDES

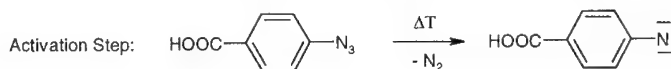
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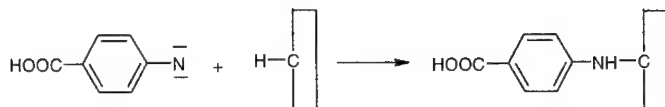
Polyolefines are limited in their application in several technologically important fields due to their low surface energy, lack of chemical functionalities, sensitivity to photo- or thermal oxidation and inadequate compatibility with other synthetic polymers. Accordingly, the chemical modification of polyolefines - the introduction of functional groups by copolymerization with polar monomers or by grafting functional monomers to the polymer backbone - has been an area of intense interest as a route to improve these commodity polymers.

The basic idea of our work was to test whether highly reactive intermediates such as nitrenes provide a useful method to functionalize polyolefines. For this purpose aromatic azides were used which are known to yield nitrenes by UV-irradiation as well as by heating. These reactive intermediates can undergo a multitude of reactions, for example, insertion into C-H, N-H and O-H bonds, addition to olefines and proton abstraction reactions to give the corresponding amine.

4-Azidobenzoic acid was synthesized, films of ethylene-propylene- and ethylene-octene-copolymers containing 1-10 wt-% azide were prepared and heated to 125-220°C.



Covalent Attachment to the Polymer:



After removing byproducts the amount of covalently bonded aminobenzoic acid was determined by titration of the carboxyl groups.

## ADHESIVE PROPERTIES OF PHOSPHORYL CHLORIDE MODIFIED POLYPROPYLENE

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A modification of isotactic polypropylene (iPP) by oxidative - chemical method results in a significant increase of the both polarity and hydrophilicity of the polymer [1,2]. Among practically important methods, halogenization is the one of the highest efficiency [3]. The procedure is based on the effect of the vapours of halogene-containing compounds or halogene itself on the iPP surface. In many cases uv irradiation is parallely used resulting in a faster decomposition of the modification compound and direct uv-oxidation of the polymer surface. The effect of halogenization agent is enhanced by such a way [4]. Most frequently applied methods include chlorosulphonation by sulphur dioxide and chlorine as well as the modification in the vapours of phosphorous trichloride [5]. UV irradiation leads to a decomposition of phosphorous trichloride and to an oxidation of the polymer at the same time.

Surface modification of polypropylene in vapours of phosphoryl chloride under uv irradiation is an effective method for the increase of adhesive properties. Phosphoryl chloride acts as the sensitizer which decomposes under the effect of uv irradiation. The active chlorine is formed during the decomposition and reacts with the polymer. At the same time a reaction with oxygen proceeds, initiated by uv irradiation, resulting in a formation of polar oxygen - containing moieties [6].

In this work the adhesive properties of the phosphoryl chloride modified polypropylene have been investigated. The polar component of the surface free energy has increased from 0.2 up to 5.6  $\text{mJ.m}^{-2}$  after 30 seconds of the modification. The increase up to 16.5  $\text{mJ.m}^{-2}$  was observed after 20 minutes modification. Mechanical work of adhesion of the phosphoryl chloride modified iPP towards polyvinyl acetate increased from 25 up to 155  $\text{mJ.m}^{-2}$  after 20 minute modification. Longer modification did not lead to further increase of the value. The adhesion parameters have been calculated from goniometric measurements of the contact angles using a set of testing liquids on the polymer surface.

The contact angles have been measured during 10 minutes in 30 second intervals. The dependence of the contact angle vs time of measurement was extrapolated to  $t = 0$ . The mechanical work of adhesion was measured by peeling experiment of adhesive joints at  $90^\circ$  using an universal testing machine INSTRON 4301. The length of the adhesive joint was 100 mm. The modification was done in the phosphoryl chloride vapours in a quartz tube while uv irradiation was emitted by Hg 400 W source being placed 100 mm from the polymer surface.

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## POLYPROPYLENE MODIFIED WITH SULPHUR DIOXIDE

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An interest in chemical modification of polypropylene (PP) continues with increasing intensity from the early beginning of PP application. A principal problem in such chemistry is activation of polymer molecules by synthesis of an initiator sites. The hydroperoxy groups serve as relatively suitable precursors for free radical reactions on PP macromolecules. These are easily generated by mild thermal oxidation or by variety of other treatments of PP including radiation or plasma procedures.

This poster describes an attachment of polar sulphate and sulphonate groups to both atactic and isotactic PP by the reaction of sulphur dioxide with oxidized PP macromolecules. The blends of PP and low molecular hydroperoxides (cumylhydroperoxide (CHP) and *t*-butylhydroperoxide (tBHP) were also used.

Oxidized PP films 0,1 mm thick were prepared by low temperature oxidation at 50°C in ozone-oxygen mixture flow of 270 ml/min. during 5 hours. The 0.094 mol/kg of peroxidic oxygen was determined in polymer films by iodometry.

The SO<sub>2</sub> forms with hydroperoxides very active redox systems capable of generation free radicals even at temperatures well below 0 °C [1]. Activated decomposition of hydroperoxides produces peroxyradicals, sulphate and sulphonate ion radicals able to combine with PP radicals and introduce to hydrocarbon macromolecules the polar functional groups [2].

The SO<sub>2</sub> treatment of oxidized PP resulted in bonding sulphate and sulphonate groups to PP macromolecules. Their concentration in atactic PP films was determined by the dye partition technique [3]. The sulphony groups concentration arises over the peroxide concentration more than 20 times as temperature increases from 10 to 70 °C. However the modification of PP by low molecular CHP or tBHP decomposed in presence of SO<sub>2</sub> is considerable less effective and represents only a fraction of 1/5 from added peroxide.

Temperature influences the addition of reaction intermediates of SO<sub>2</sub> and hydroperoxide to oxidized PP with coefficient of 40 kJ/mol. This value shows on increasing hydrogen transfer reactions of free radicals with PP.

The modified isotactic PP foils and fabrics have better dyability and are better wetted by polar solvents compared to starting polymer.

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Table I. The contact angles  $\Theta$  of H<sub>2</sub>O on PP films press moulded from PP powders modified by 20 fold molar excess of pure SO<sub>2</sub> gas at 60 °C, 30 min in dependence on concentration of CHP in PP grains.

CHP [wt %]	< $\Theta$ °; SD *	
starting polymer	71.6	1.10
0.5	62.4	1.28
1.0	61.0	1.60
2.0	59.2	1.44
5.0	57.4	1.12
10.0	55.8	1.04

Table II. The contact angles  $\Theta$  of H<sub>2</sub>O on PP films press moulded from PP powders modified by 20 fold molar excess of pure SO<sub>2</sub> gas during 30 min and 5 wt % of tBHP in dependence on temperature.

T [°C]	< $\Theta$ °; SD *	
starting polymer	71.6	1.10
-10	55.2	0.96
20	48.4	4.32
60	46.8	2.84
120	46.0	1.40

\* Standard Deviation

## OLEFIN POLYMERIZATION WITH SUPPORTED METALLOCENE CATALYSTS

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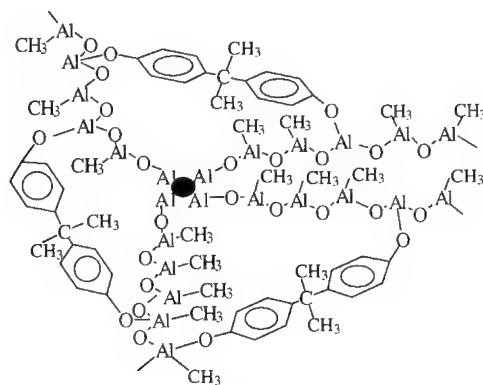
Metallocene catalysts in dissolved form are unsuitable for the production of polyolefines on an industrial scale. The commercial application of soluble metallocene catalysts would require the design of new plants or the adaptation of existing ones to operate with soluble catalysts. One way of overcoming this problem is to support them on various "inert" carriers. Metallocene can be supported on several inorganic oxides, the most commonly used being  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and several magnesium compounds, different methods are possible. The isoselective propene polymerization using the supported zirconocene/ methylalumoxane catalysts were investigated.

For our investigations we used various inorganic oxides treated with crosslinked MAO\* (1).

The type of the support as well as the technique used for supporting the metallocene and MAO have a crucial influence on catalyst behavior.

We carried out some polymerizations with this catalysts and determined relative activities and some kinetic parameters.

Further we studied the behavior of the supported metallocene catalysts in comparison to a commercial Ziegler Natta catalyst, especially with respect to activity and catalyst surface. We carried out the polymerizations in a solvent and as bulk-polymerization in liquid monomer.



(1)

●  $\text{Al}_2\text{O}_3$  grain

\* Patent PCD EPA 0685494

### STRUCTURE AND PROPERTIES OF ETHYLENE COPOLYMERS SYNTHESIZED BY METALLOCENE CATALYSTS

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With metallocene catalysts it is possible to synthesize ethylene copolymers with narrow molecular weight distribution and homogeneous chemical composition. Crystallinity, melting temperature, and density of the PE are reduced by the comonomer incorporation. With increasing comonomer content low density polyethylene and highly flexible copolymers (polyolefin elastomers) are obtained. Correlations between catalyst and copolymerization behavior are described in literature widely, while influences on morphology, mechanical and rheological properties of mLLDPEs is hardly studied. Although the homogeneity of the copolymers has an extremely positive effect on their profile of use, it is supposed to complicate the processing.

Therefore, we investigated these relationships in ethylene copolymers based on 1-hexene, 1-octene, and norbornene as comonomers. The copolymers were synthesized with a comonomer content ranged from 0 to about 12 mol%.  $[\text{Me}_2\text{C}(\text{3-tBuCp})(\text{Flu})]\text{ZrCl}_2/\text{MAO}$  was used as catalyst for the copolymerizations of ethylene and 1-hexene and of ethylene and 1-octene.  $[\text{Me}_2\text{C}(\text{3-MeCp})(\text{Flu})]\text{ZrCl}_2/\text{MAO}$  and  $[\text{Me}_2\text{C}(\text{3-tBuCp})(\text{Flu})]\text{ZrCl}_2/\text{MAO}$  were used as catalysts for the ethylene-norbornene copolymerization. Ethylene-norbornene copolymers produced by  $[\text{Me}_2\text{C}(\text{3-tBuCp})(\text{Flu})]\text{ZrCl}_2$  were shown to feature a microstructure containing only odd numbered ethene sequence lengths, while those produced by  $[\text{Me}_2\text{C}(\text{3-MeCp})(\text{Flu})]\text{ZrCl}_2$  show a statistical distribution of odd and even numbered ethene sequence lengths.

The microstructure of the copolymers was studied and related to its melting, crystallization, and glass transition behavior as well as to selected mechanical properties.



## MORPHOLOGY AND DEGRADATION BEHAVIOR OF IPN BASED ON POLYETHYLENE AND POLYMETHACRYLATES

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Interpenetrating polymeric networks (IPN) based on polyethylene (PE) and polymethacrylates differ strongly in their phase morphology which can be adjusted by variation of the compositions of the IPN and the synthesis conditions [1]. In this type of IPN the PE phase forms a continuous network like phase surrounding spherical particles formed from the polymethacrylates [1,2]. Since the two components of the IPN, i.e. PE and polymethacrylate, behave quite different under electron beam radiation, it should be possible to create polymeric porous materials by treating the IPN materials with electron beam radiation: polyethylene crosslinks whereas polymethacrylates degrade. The purpose of this project is to study the possibility of preparing membranes from such irradiated IPN structure.

Thin IPN films composed of polyethylene and polymethacrylates were synthesized by *in situ* method [3] in a plate reactor. Linear low density polyethylene (LLDPE) was used in powder form, and methyl (MMA), ethyl (EMA), butyl (BMA), and dodecyl (DMA) methacrylates were used for the preparation of the polymethacrylate phase.

The crosslinking of LLDPE both by electron beam and by peroxide was investigated in terms of gel content. The degradation behavior of individual polymethacrylates was studied in the immediate presence of polyethylene by a gravimetric method. All of the investigated polymethacrylates degrade more than crosslink independent of the length of the ester side groups (Fig. 1). Surprisingly, a notable degradation of PE/poly(dodecyl methacrylate) by irradiation was also found, which is inconsistent with results reported for pure poly(dodecyl methacrylate) [4].

Scanning electron microscope (SEM) was used to observe morphology changes in the irradiated samples. Pores of about 200 to 400 nm in diameter were observed on the surface (Fig. 2) and in the bulk phase of irradiated IPN. Flux measurement showed that some irradiated samples were permeable to ethanol, indicating an open porous structure which may be relevant for membranes.

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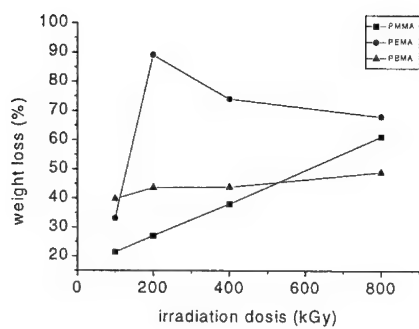


Fig. 1 Weight loss of polymethacrylates after extraction with xylene in dependence of irradiation doses

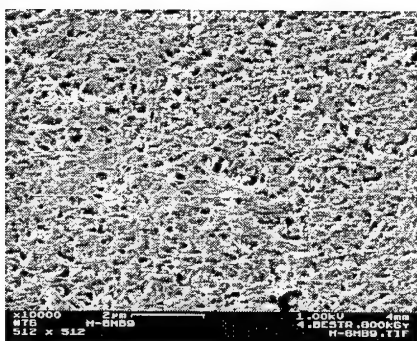


Fig. 2 Electron micrograph of irradiated (800 kGy) surface of PE/BMA-co-EMA after extraction with xylene

## EFFECT OF COMPONENT INTERACTION ON THE MELTING AND CRYSTALLIZATION CHARACTERISTICS OF PE/PIB BLENDS

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Commodity polymers are often combined with each other in order to achieve improved processability, barrier properties or simply to decrease price. Polyolefins are also blended with other polymers to improve the properties of various films used for packaging. A certain compatibility of the components is the minimum condition for achieving acceptable properties. Interaction of the components usually takes place in the amorphous phases of the polymers, but in the case of miscibility also the crystalline structure is modified. According to numerous literature references, conclusions can be drawn about the miscibility of the components from the extent of the changes in the melting and crystallization characteristics of a polymer.

In a series of experiments high density polyethylene(PE)/polyisobutylene (PIB) blends were prepared in the whole composition range. PIB content of the blends changed from 0 to 1 volume fraction in 0.1 volume fraction steps. The components were homogenized in an internal mixer at 150 °C for 10 min. 1 mm thick plates were compression molded at 150 °C. Mechanical characterization was carried out by tensile testing and dynamic mechanical spectroscopy. Melting and crystallization characteristics of the PE component were determined in non-isothermal and isothermal experiments. In non-isothermal measurements the sample was heated up to 160 °C with a rate of 10 °C/min than cooled down to room temperature with rates of 40, 20, 10, 5 and 2.5 °C/min, respectively. Isothermal crystallization was carried out at various temperatures and the equilibrium melting temperature was determined.

Crystallization and melting characteristics were evaluated as a function of composition. Significant changes were observed in them at high polyisobutylene contents. An attempt was made to calculate the Frory-Huggins interaction parameter from the equilibrium melting temperature [1]. The results were compared to values obtained from DSC measurements and dynamic mechanical spectroscopy [2]. All the experiments showed that estimation of miscibility in polyethylene blends is very difficult. These difficulties originate partly in the crystalline structure of the polymer and partly in the lack of specific interactions. Also technical problems often arise during the experiments, the small changes in the characteristics require accurate measurements. Nevertheless, the parameters derived by the different techniques showed acceptable agreement and indicated a certain degree of interaction in the PE/PIB blends studied.

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## ADHESION OF MODIFIED PE/EPDM BLENDS TO STEEL

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Controllable contact oxidation is proved to be an efficient development technique of strength and durability of adhesive joints between polyolefins (PO) and steel [1,2]. PO are modified for this reason by specific additives (sorptive fillers, organic peroxides etc.). Thermal contact of PO containing these additives at certain environment-temperature-time conditions guarantee optimal equilibrium of kinetics of oxygen containing groups formation, oxidative destruction and cross-linking. This leads to significant improvement of PO adhesiveness as well as strengthening of weak boundary layer of polymer.

The progress in the improvement of the cohesive and adhesive characteristics of LDPE and HDPE blends with ethylene-propylene-diene terpolymer (EPDM) cross-linked by dicumyl peroxide (DCP) in the presence of metallic coagent - Zn diacrylate (*Saret* 633) is reported. This complex cross-linking system (CCS) is known as efficient additive for the improving of mechanical properties of saturated and unsaturated elastomers as well as in strengthening of adhesive joints of vulcanised rubber to metal [3].

Cohesive characteristics and peel strength (A) adhesive joints with cold rolled steel foil can be substantially considerably improved for blends modified by CCS (see Figure as an example).

*Saret* obviously promotes oxidative cross-linking within boundary layer of PO, which is main reason of peel strength growth. Visually adhesive mode of fracture of adhesive joints with in fact is cohesive within thin boundary layer (less than 1  $\mu\text{m}$ ).

Studies of contact process of cross-linking agents containing LDPE/EPDM and HDPE/EPDM blends by DSC allows to observe two separate exothermic peaks. One of them (with a maximum at 177 - 183  $^{\circ}\text{C}$ ) corresponds to peroxide cross-linking heat effect. Another one (with a maximum at 229 - 250  $^{\circ}\text{C}$ ) is heat effect of intensive contact oxidation.

There is sufficient increase in peroxide cross-linking heat effect in presence of *Saret*. *Saret* alone does not act as cross-linking agent at all. Simultaneously *Saret* influences contact oxidation and acts as a peculiar stabiliser: there is remarkable decrease in the heat effect of intensive contact oxidation and drop of maximum temperature of this process in presence of *Saret*.

Efficiency of *Saret* as adhesion promoter is very sensitive to thermal prehistory of adhesive preparation. The best results can be gained in a case when composition is used as adhesive just after thermoplastic mixing (roll mixer). Subsequent hot pressing leads to significant reduction of adhesiveness due to premature cross-linking.

Water resistance studies of adhesive joints of CCS containing LDPE/EPDM blends with steel shows sharp drop of peel strength at first few days of exposure of adhesive joints in hot (90  $^{\circ}\text{C}$ ) water from initial peel strength 6.0 - 12.0 kN/m. After it peel strength values stabilises on the level 1.0 - 1.5 kN/m. The identical studies for HDPE/EPDM blends, which characterises by comparatively low initial peel strength (2.0 - 3.0 kN/m) exhibits the same stable level for more than 300 hours of exposure in hot water.

Studies carried out demonstrates that complex cross-linking system DCP/*Saret* can be used for guarantying of relatively strong adhesive bond between PE/EPDM blend and steel.

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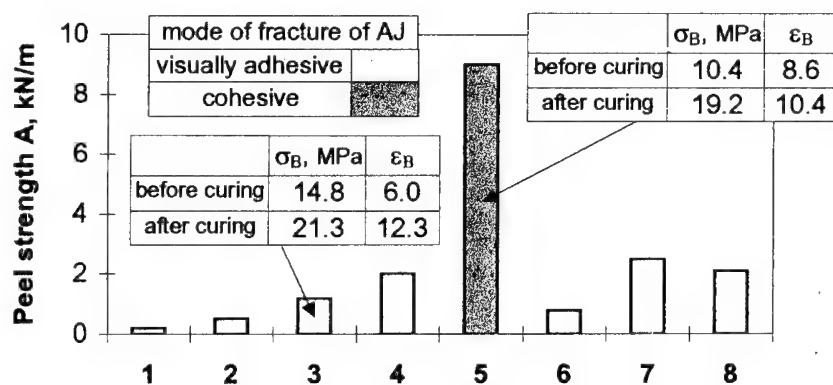


Figure. Some strength-deformation characteristics ( $\sigma_B$  - tensile strength,  $\varepsilon_B$  - elongation at break) and peel strength A of adhesive joints with steel (contact at 180°C for 3 min) of cross-linked systems:

- 1 - LDPE, 2 - LDPE + 20% EPDM,
- 3 - LDPE + 1% DCP, 4 - LDPE + 1% DCP + 1% Saret,
- 5 - LDPE + 20% EPDM + 1% DCP + 1% Saret,
- 6 - HDPE + 1% DCP, 7 - HDPE + 20% EPDM + 1% DCP + 1% Saret,
- 8 - EPDM + 1% DCP + 1% Saret

## RADIOCHEMICAL PROCESSING OF EPDM/NR BLENDS

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Gamma irradiation of binary blends of EPDM (containing ethylidene norbornene as added diene) and natural rubber was performed in order to provide a radiochemical technology for the intimate blending of these components. The large range of mixing ratio was covered, namely individual components, 3:1, 1:1 and 1:3 (w/w).

Gel content was measured by refluxing in o-xylene for 24 h. The greater proportion of natural rubber decreases the level of crosslinked fraction. It means that the rate of scission exceeds those of crosslinking. Otherwise, the changes in soluble fraction of 3:1 and 1:1 (EPDM/NR) prove the main contribution of network formation.

It is well known that thermal stability of ethylene-propylene terpolymer and natural rubber are quite unlike. Figure 1 present the dependencies of oxygen uptake on time for two temperatures. It can be noticed that the rate of oxidation for this kind of blends depends not only on mixing ratio but also on test temperature.

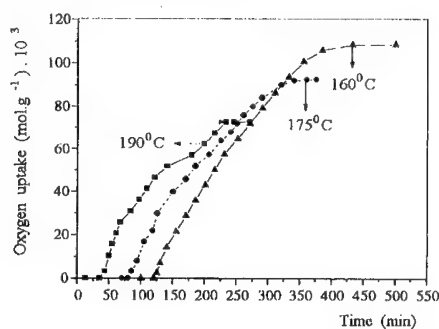


Fig. 1 Time dependencies of oxygen uptake on testing time at two temperatures.  
Samples EPDM/NR = 3:1 (unirradiated)

Irradiated polymer blends are subjected to molecular scission. EPDM belongs to crosslinking polymers, while natural rubber shows remarkable rate of degradation. Such systems can be crosslinked, when the amount of synthetic elastomer exceeds 50 %. It can be assumed that free radicals provided by natural rubber component would be grafted on the EPDM.

Radiation behaviour of these systems is described by various reactions which are jointed in mechanism of crosslinking based on gel content determinations and oxygen uptake measurements.

## DYED GRAFTED POLYPROPYLENE FILMS FOR HIGH - DOSE RADIATION DOSIMETRY

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Gamma Radiation - induced polymerization of acrylic acid (AAc) onto polypropylene (PP) film has been carried out under nitrogen atmosphere. The obtained grafted film of PP- g - PAAc was allowed to react with two ionic dyes, namely malachite green (MALG ) or methylene green (METG). The carried out investigations showed that new dosimeter films of PPMALG and PPMETG have been developed for high - dose gamma radiation applications. The useful dose range of these films extends up to about 400 kGy, with a minimum useful dose of about 5 kGy. The radiation - induced colour bleaching has been analyzed with visible spectrophotometry.

The radiolytic bleaching of alcohol solutions of triphenyl methane dyes ( e.g. Malachite Green ) has been shown to be promising for dosimetry in the dose range 10 to  $2 \cdot 10^3$  Gy [R]. After prepare films of grafted acrylic acid onto PP and subjecting them to dyeing by two ionic dyes, Malachite Green (MALG) and Methylene Green (METG) are investigated for their eventual application as radiation dosimeters.

Saturated polymers such as polypropylene are usually resistant to direct dyeing, this difficulty can however, be overcome by grafting suitable branches onto the backbone of PP macromolecules, this may be accomplished by grafting at first acrylic acid onto polypropylene and then subjecting the obtained graft - copolymer of PP - g - PAAc to the dye material (such technique was proved by our laboratory) .

Irradiation was carried out by using 60 Co gamma chamber Dose rate 3.67 kGy/h.

The absorption spectra of both PPMEG and PPMALG at 601, 429 nm and 623, 429 nm measured respectively at different Doses ( Fig. 1,2 ), ( Fig. 3 ) shows the change

of  $(\Delta A/\Delta A_0)_\lambda$  values at 601 and 623 nm as a function of absorbed Dose for both days.

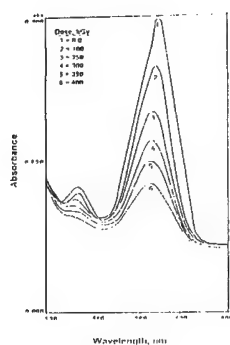


Figure 1.

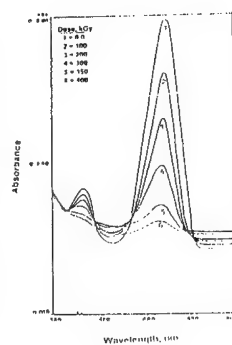


Figure 2.

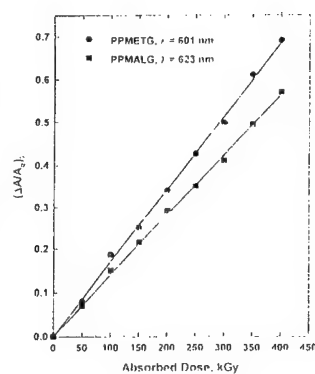


Figure 3.

These two lines may be demonstrated by the following relationships:

$$\text{Dose} = 707.72 (\Delta A/A_0)_{601}$$

$$\text{Dose} = 583.75 (\Delta A/A_0)_{623}$$

The effects of relative humidity during irradiation, shelf-life and post-irradiation storage in dark and indirect daylight conditions on dosimeters performance are discussed.

These films can be produced in large quantities and inexpensively which make them suitable for high-dose applications as routine dosimeters in Radiation processing.



**COPOLYMERIZATION AND CHARACTERIZATION OF  
END-ALLENOXY OXYETHYLENES WITH N-VINYL-2-PYRROLIDONE**

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The radical copolymerization of monoethylene glycol allenyl methyl ether (MEGA), with N-vinyl pyrrolidone (VP) were investigated at various composition using AIBN as initiator at 60 °C.

The composition of the copolymers were characterized by  $^1\text{H}$  NMR, IR and GPC techniques. Values of reactivity ratios were determined using NMR methods,  $r_1$  (MEGA) =  $0.41 \pm 0.05$  and  $r_2$  (VP) =  $0.765 \pm 0.08$  calculated. Thermal stabilities and degradation behaviours of the polymers were examined using TG/DTG methods. The thermal stabilities of the copolymers were intermediated between those of the tow homopolymers, and appear to degrade in two stages. The first stage resulting from decomposition of C-O bonds of the side chain and the C -C bond  $\beta$  to double bonds of PMEGA units. The second stage resulted from the decomposition of the pyrrolidone ring of PVP units.

**SOME PROPERTIES OF BLENDS BASED ON HIGH DENSITY  
POLYETHYLENE AND LOW DENSITY POLYETHYLENE GRAFTED  
WITH DI-2-ETHYLHEXYL FUMARATE**

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In this paper blends based on high density polyethylene (MFI=0.3 g/10 min) made in Romania and low density polyethylene grafted with di-2-ethyl-hexyl fumarate (EHF) are presented.

The above mentioned blends were obtained through component homogenization, in different proportions, on a Berstorff laboratory roll-mill, for 10 minutes at 180°C.

Low density polyethylene (MFI=2.0 g/10 min) grafting with di-2-ethyl-hexyl fumarate was carried out in polymer melt, through radicalic initiation, in the presence of organic peroxides, at a temperature of 140-160 °C. Grafted polyethylene obtained in this way was purified through extraction for taking off the unreacted monomer. The content of grafted monomer was determined through IR absorption spectrophotometry using the absorption band of 1735 cm<sup>-1</sup> generated by elongation vibration of C=O group of esteric type.

Plates were manufactured from these blends, at a temperature of 180 °C and a pressure of 300 bars with the purpose of determining the main physical-mechanical characteristics. Melt flow index (MFI) and tensile properties evolution were followed.

The results obtained experimentally emphasize the important decrease of MFI at small contents of grafted monomer (1,5-2,5% gr EHF) and then the increase of these one. The tensile properties determined for the studied blends suffered important changes. Thus, tensile strength shows an increase with the content of grafted monomer (1,5-2% gr EHF) and then a decrease of the values. Elongation at break of the respective blends has an uniform increase with the content of grafted EHF.

The obtained blends were characterized through optical microscopy and the modification of crystalline structure due to the presence of modified polymer through grafting were emphasized.

The main characteristic evolution of the studied blends allowed the outline of some utilisation proposals of these ones.

# AMPHIPATHIC COPOLYMER AS STABILIZER FOR EMULSION POLYMERIZATION OF STYRENE MONOMER

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## Abstract

The emulsion polymerization of styrene monomer (St.) initiated by sodium persulphate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) as an initiator has been kinetically investigated in the presence of prepared amphipathic copolymer as stabilizer. Amphipathic copolymer of three different composition types from vinyl acetate monomer and methoxy polyoxyethylene (PVAc-b-MPOE) (35:65 , 27:73 , 19:81 wt% : wt%) were prepared in presence of benzoyl peroxide using a macroradical initiator techniques. Fourier Transform Infrared spectroscopy (FTIR) and  $^1\text{H}$  NMR were carried out to confirm the structure of the obtained copolymer.

The rate of emulsion polymerization of styrene monomer was found to be proportional to the  $0.33^{\text{rd}}$  ,  $0.375^{\text{rd}}$  and,  $0.385^{\text{rd}}$  power of the emulsifier (amphipathic) concentration  $[\text{E}]$  and to the  $0.67^{\text{th}}$  ,  $0.71^{\text{th}}$  and  $0.8^{\text{th}}$  power of the initiator concentrations  $[\text{I}]$ . The apparent activation energy is found to be 91.7, 81.9 and 71.6 kJ/mol for 65 wt% , 73 wt% and 81 wt% POE respectively. It is observed that number average particle diameter ( $D_n$ ) decreases with increasing amphipathic  $[\text{E}]$  while increases with  $[\text{I}]$ . The number of polymer particle ( $N_t$ ) increasing with amphipathic concentrations but decrease with initiator concentrations. The reaction order ( $N_t$  versus  $[\text{E}]$ ) was investigated. Polydispersity index ( $D_w/D_n$ ) was found in the range from 1.05-1.20 with changing POE wt% in amphipathic copolymer concentrations and from 0.8 to 1.23 with initiator concentrations.

**STRUCTURE DEVELOPMENT DURING FLOW OF TERNARY BLENDS OF A OF  
A POLYAMIDE (NYLON 66), A THERMOTROPIC LIQUID CRYSTALLINE  
POLYMER (POLY(ESTER AMIDE)) AND A FUNCTIONALIZED  
POLYPROPYLENE**

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We investigated the possible deformation and fibril formation of TLCP (VB) in nylon 66 matrix whose viscosity is lower than that of VB, by adding a small amount of functional polypropylene whose functional group ( maleic anhydride) can react with end groups(amines) of nylon 66 and VB to produce graft-block copolymers that act as the compatibilizer at the interface. Addition of a third component, a functionalized polypropylene (maleic anhydride grafted polypropylene, MA-PP) that interacts with the matrix polymer (nylon 66) and the thermotropic liquid crystalline polymer facilitates the structural development of the TLCP by acting as a compatibilizer at the interface. When a proper amount of the compatibilizer is added, some fine fibrils are formed in the ternary blend system even without strong elongational drawing. Morphological observation determined the significance of compatibilization in immiscible polymer blends. The compatibilizer brings about good adhesion at the interface, reduces the droplet size, and enables finely dispersed liquid crystalline polymer to be deformed in shear flow without strong elongation even though the viscosity of the matrix was much lower than that of the liquid crystalline polymer. Good adhesion at the interface is believed to promote efficient stress transfer to deform TLCP droplets which are in the melt state at the processing temperature. This result corroborates that the interfacial adhesion and the size of dispersed droplets are as much the decisive factors as the viscosity ratio of the TLCP to that of the isotropic polymer in determining the deformation and structure development of the TLCP phase.

Mechanical properties of the ternary blends compared to those of the binary blend were increased. This is ascribed to the fibril generation induced by the addition of MA-PP. Enhanced adhesion at the interface improved elongation in the ternary blends. The improvement of mechanical properties (elongation at peak as well as tensile strength and modulus ) are remarkable when the proper amount of MA-PP is added, which enables improved adhesion at the interface. The loss of ductility of nylon 66 by the addition of VB is ascribed to the incompatibility of those two which can be improved by the addition of MA-PP. It may be also partly attributed to degradation of added MA-PP at high temperature. Optimum amount of the compatibilizer is the key for the best morphology and hence for the best mechanical properties.

## PP/GLASS WEFT KNITTED STRUCTURES FOR COMPOSITES

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Knitted textile fabrics, especially weft knitted fabrics, have well known properties of elasticity, soft touch, low bulk density and drapeability. All those properties make them suitable for garment production. Beside the garment production, for the last few years, the knitted structure have been used as preforms in production of textile structural composites.

These preforms contain reinforcing fibre and matrix fibre which have different physical and mechanical properties. The knitted textile structures for composite production offer some advantages, such as: economical production, easy handling, short time of impregnation, easy managing with reinforcement/matrix fibre mass ratio etc.

The weft knitted rib structures were processed on the flat knitting machine with various machine gauge. The samples were knitted from Side by side type of hybrid yarn. The hybrid yarn contained PP yarn and glass yarn in the mass ratio PP/glass = 2/1. The overall yarn count of hybrid yarn was 450 tex. During knitting, the yarn input tension and sinking depth were varied. Therefore, the knitted samples with various mass per square meter were obtained (300 - 1800 g/m<sup>2</sup>).

Consolidation of the preforms was performed on the seem-industrial press by thermocompression under controlled condition at 200 and 225 °C..

The following tests were carried out at test specimens: Tensile test; Bending test and Impact test.

It was found that the content of the reinforcing fibre increases with increasing the stitch density. Also tensile and bending properties increase with increasing the stitch density due to higher content of reinforcing fibre. Generally the composites have superior properties in longitudinal direction.

The void content influences the composites mechanical properties. Increasing the void content for 5%, decrease the bending force for 20-25%.

Increasing the time of impregnation up to 20 min increases the bending force and bending modulus. Higher time of impregnation doesn't influence the mechanical properties of composites.

Composites processed at 200 °C showed better mechanical properties than composites processed at 225 °C..

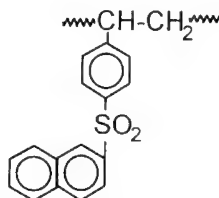
# SYNTHESIS AND INVESTIGATION OF THERMODYNAMIC PROPERTIES OF POLY (2-NAPHTHALANE SULPHONYL) STYRENE

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Polystyrene has been sulphonylated by reaction with 2-naphthalene sulphonylchloride in dichloromethane at room temperature in presence of anhydrous aluminium chloride. The sulphonylated polystyrene (PNS) has been characterized by  $^{13}\text{C}$ ,  $^1\text{H}$ -NMR and FT-IR techniques. DSC thermogram showed that the glass transition temperature is about 137 °C for the PNS.



Some thermodynamic parameters such as average partial molar enthalpy  $\Delta H_1^\infty$ , partial molar free energy  $\Delta G_1^\infty$ , weight fraction activity coefficient  $\Omega_1^\infty$  and Flory-Huggins interaction parameter  $\chi$  for PNS organic solvents systems at infinite dilution were found by using the i.g.c. technique. Also, the solubility parameter of PNS at infinite dilution was found by plotting the graph  $[(\delta_1^2/RT) - \chi/V_1]$  versus solubility parameters of organic solvents ( $\delta_1$ ).

## BEHAVIOUR OF CHLOROSULFONATED POLYETHYLENE ON GAMMA RADIATION

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The initial properties of polyethylene are changed by chlorosulfonation and subsequently results an elastomer with intrinsic stability against various atmospheric factors, chemical agents in a rather large domain of temperature. Due to its performances, chlorosulfonated polyethylene (CSM) is the elastomer of choice for a big range of applications including seals, gaskets linings and cable sheetings in nuclear energetics [1 ; 4].

In the present work, the behaviour of CSM on irradiation supplied by a Cs<sup>137</sup> source was investigated in the range of total absorbed dose of 5 - 500 kGy. Two types of CSM were used: *Hypalon 40* (Du Pont de Nemours, USA) and *Carom CSM* (Chimcomplex SA, Romania) with main characteristics grouped in Table 1.

Table 1

The characteristics of the investigated CSMs

Elastomer type	Chlorine content, %	Sulfur content, %	Unsaturation, %	Gel content, %
Hypalon 40	36.0	1.2	0.75	nil
Carom CSM	33.8	1.3	0.40	nil

The exposure to high energy radiation was realized at room temperature taking into account the following aspects: (i) structural modifications of the polymer as revealed by infrared spectra; (ii) variation of gel content using the method [5]; (iii) variation of chlorine and sulfur content [6]; (iv) determination of the hydrochloric acid splitted from polymer; (v) modification of unsaturation degree [7].

As a result of irradiation, some changes take place, the most important being observed in regions 3600 - 3200 cm<sup>-1</sup> and 1800 - 1650 cm<sup>-1</sup>, where come visible formation and evolution of OOH/OH and C=O groups.

The evolution of C=O groups is presented in Figure 2.

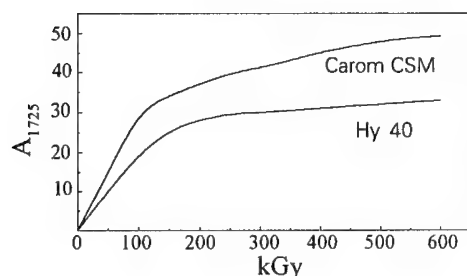


Figure 2  
The evolution of carbonyl content  
vs. absorbed dose

At the same time, after exposure at various doses, the modification of the bands at 1370 and 1155  $\text{cm}^{-1}$  assigned to  $\delta\text{SO}_2\text{Cl}$  and  $\delta\text{SO}_2$  groups were observed demonstrating that the chlorosulfonic group is quite sensitive to radiation. The evolution of ratio E1370/E1460 shows that the decrease of  $\text{SO}_2\text{Cl}$  content is more enhanced up to 100 kGy after that its content remains at a rather constant level.

For the both polymers, the evolution of the unsaturation increases monotonously up to a dose of 50 - 100 kGy and then decreases to a level lower than initial. The gel content starts with low absorbed dose (20 kGy) and its evolution is dissimilar for the two polymers; thus Hypalon 40 is completely crosslinked at 200 kGy and Carom CSM is crosslinked at 350 kGy.

During exposure on radiation, the content of chlorine and sulfur decreases continuously reaching at the maximal dose to lose 20 - 32 % and 6,5 - 8 % respectively.

The obtained data made render evident the complexity of the process. The main changes consist in:

- radiation exposure leads to the splitting of chlorine and chlorosulfonic groups with formation of hydrochloric acid and sulfur dioxide accompanied by formation of free macroradicals and C=C units;
- free macroradicals are able to react with atmospheric oxygen leading to various oxygen-bearing structures and to crosslinking of the polymer.

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**MODIFICATIONS OF MICROSTRUCTURAL AND MECHANICAL  
PROPERTIES OF POLYETHYLENE INDUCED BY COLD-ROLLING  
AND THERMAL TREATMENTS**

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Modifications of microstructural and mechanical properties of polyethylene (PE) have been studied by many authors, but nearly always on drawn polymers (1-5). Only a few papers deal with rolling of polymers (6-7). The aim of this work is to study, on the one hand, the changes in morphological and mechanical properties due to cold-rolling, and on the other hand, the evolution of these same properties with thermal treatment after cold-rolling.

A series of high density polyethylene (HDPE) of variable rolling ratio (0-390%) is analysed by X-ray diffraction and scanning electron microscopy (SEM).

During cold-rolling, the crystalline lattice is partly transformed from orthorhombic to monoclinic structure. This transformation is reversible when the material is annealed at 140°C during one hour.

A great diminution of the size of the spherulites is observed by SEM during rolling, but this treatment seems to give morphology difference between the surface and the core of the sample.

Mechanical properties are analysed with tensile tests. The deformation energy per unit volume is highly increased by rolling (from 2MPa to 27MPa) due to either the rise of the number of connections between crystalline and amorphous phases, or the increase of Van der Waals forces (8).

Contrary to the modification of the crystalline lattice, the changes of morphological and mechanical properties are not reversible.

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## MECHANICAL PROPERTIES OF PP/HDPE/EPR BLENDS WITH CALCIUM CARBONATE

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### INTRODUCTION

The interest in developing mixtures of polyolefins resides in the fact that these materials represent a high percentage of the plastic waste at world level<sup>1</sup>. The incorporation of High Density Polyethylene and ethylene-propylene copolymers (EPR) in Polypropylene improves the mechanical behavior of the pure Polypropylene<sup>1-2</sup>. Although numerous studies of calcium carbonate filled PP<sup>3-5</sup> have been carried out few of those report the use of this filler in PP/HDPE blends<sup>1</sup>. Furthermore, in most of them the mixing equipment has been used improperly. In this work, mixtures of PP/HDPE/EPR with CaCO<sub>3</sub> with and without titanate type coupling agent (LICA 12) were made. The homopolymers were selected in function of their rheological characteristics at the processing conditions of a corotating twin screw extruder. The optimization of blending in only one step as well as homogeneity in the filler incorporation was achieved.

### EXPERIMENTAL

A PP (supplied by PROPILVEN) and a HDPE (supplied by RESILIN) were used in a 80/20 proportion. As a modifier of the blends, an ethylene-propylene copolymer (EPR) was employed in 5 wt% respect to the mixture. CaCO<sub>3</sub> was used at 30 wt% with and without 1 wt% of LICA 12<sup>5</sup>. Some important characteristics of the materials are shown in table 1. Mixing was accomplished in one and two stages in a intermeshing co-rotating twin screw extruder made by W&P. For those blends made in of two stages, the homopolymers were mixed first and in a second extrusion the filler was then added. In the process of one single stage, all the materials were mixed simultaneously. In both cases, the filler was incorporated in a additional feed port located in a zone of the extruder where complete fusion of the homopolymers was guaranteed.

Table 1. Characteristics of the polymers and filler.

Type	Density (g/cm <sup>3</sup> )	Particle Size (μm)	Specific surface (m <sup>2</sup> /g)	MFI (g/10 min)
PP	0.91	-----	-----	7.0 <sup>a</sup>
HDPE	0.96	-----	-----	7.3 <sup>b</sup>
CaCO <sub>3</sub>	2.70	5	6.4	-----

<sup>a</sup> 230 °C, 21.6 N load; <sup>b</sup> 190 °C, 21.6N load.

## RESULTS AND DISCUSSION

The results obtained from the mechanical tests are reported in table 2. Upon incorporating the filler into virgin PP is obtained due to a decrease in the rigidization the system. However, it can be observed that with the impact resistance are improved slightly when the filler is treated with LICA 12. At break when the blends of PP/HDPE/EPR with and without filler are compared to those equivalents of virgin PP, better properties are observed.

In the blends with treated filler made in only one step an increase in the impact resistance with respect to those with untreated filler. Upon comparing the blends accomplished in one stage (5 and 6) with the similar blends accomplished in two stages (7 and 8) improvements in the elongation at break and in the impact resistance were obtained and above all the dispersion of the values of this last property was substantially smaller. Also, wasn't pointing out that the values of the properties of the blend made incorporating all the components through the hopper resulted with a high dispersion and for that reason are not reported here.

**Table 2. Properties of Polypropylene, PP/HDPE/EPR and Its Composites.**

Serial N°	Property/Sample	Modulus (MPa)	Tensile strength (MPa $\pm$ 1)	Elongation at break (%)	Izod impact strength (J/m <sup>2</sup> )
1	PP	1710 $\pm$ 70	25	> 400	2342 $\pm$ 373
2	PP/CaCO <sub>3</sub> wt	1930 $\pm$ 80	25	29.0 $\pm$ 9.9	1650 $\pm$ 567
3	PP/CaCO <sub>3</sub> t	2431 $\pm$ 98	24	34.0 $\pm$ 5.2	1923 $\pm$ 240
4	PP/HDPE/EPR	1639 $\pm$ 253	38	12.2 $\pm$ 1.2	3712 $\pm$ 504
5	PP/HDPE/EPR/CaCO <sub>3</sub> wt	2855 $\pm$ 51	27	17.5 $\pm$ 2.5	2194 $\pm$ 198
6	PP/HDPE/EPR/CaCO <sub>3</sub> t	2065 $\pm$ 300	30	12.4 $\pm$ 3.3	2244 $\pm$ 229
7	PP/HDPE/EPR/CaCO <sub>3</sub> wt <sup>†</sup>	1794 $\pm$ 30	30	13.8 $\pm$ 2.4	2038 $\pm$ 577
8	PP/HDPE/EPR/CaCO <sub>3</sub> t <sup>†</sup>	2290 $\pm$ 75	29	11.4 $\pm$ 2.7	1700 $\pm$ 528

<sup>†</sup> in two step; wt: untreated; t: treated.

## CONCLUSIONS

The mixing can be accomplished in a single stage, because the properties showed a good uniformity and substantial savings in time and in processing costs are obtained. The blends with or without filler showed better mechanical properties than the pure PP with or without filler. The treatment of filler with improves the impact resistance of the blends.

## ACKNOWLEDGEMENT

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## MECHANICAL PROPERTIES OF SHORT SISAL FIBER-REINFORCED PP AND POLYPROPYLENE-g-DEM

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### INTRODUCTION

During the two last decades, natural fibers such as jute, sisal and henequen have been widely used in different applications as twisted threads for cords and different woven textiles. Furthermore, those natural short fibers seem to be a reinforcement alternative compared to other fibers because of their good mechanical strength and processability and low cost and density<sup>1</sup>. It is well known that the mechanical properties of reinforced materials depend on the concentration of the fiber, its dispersion in the thermoplastic matrix, the individual properties of the components and on their interface compatibility<sup>2,3,4</sup>. Natural fiber incorporation into an inert polymer as the polypropylene requires whether it be a pretreatment of the fibers<sup>5</sup> or the use of coupling agents<sup>6</sup>.

In this study, the mechanical properties of composites obtained by different combinations of acetylated and untreated short sisal fiber (Agave sisalana) with polypropylene and polypropylene-g-DEM were evaluated.

### EXPERIMENTAL

Two polypropylenes PP1 (11.6 g/10 min) and PP2 (1.4 g/10 min) supplied by PROPILVEN were employed. The PP2 was functionalized via extrusion with diethylmaleate (6 phr) and dicumyl peroxide (0.05 phr) and polymer with a MFI of 17.7 g/10 min was then obtained. Sisal fiber (Agave sisalana) was used as filler. It was cut in a mill to an average length of 10 mm. The fiber was washed with water several times and then dried at 70 °C for 1.5 hours. The acetylation of the fiber was accomplished following the procedure described by Varghese<sup>7</sup>. The composites were prepared in a intermeshing co-rotating twin screw extruder and then injection molded. The tensile properties and for the Izod impact resistance were evaluated following ASTM D 638 and ASTM D 256, respectively.

### RESULTS

The mechanical properties of the composites are summarized in table 1. The diethylmaleate modified PP (PP2-g-DEM) showed higher impact resistance than the PP did, even though the modified had a lower molecular weight, due to chain scission that occurred during the functionalization via extrusion. A lower viscosity

curve was obtained for the grafted polypropylene in a capillary rheometer. Composites containing short sisal fiber showed superior mechanical performance than the PP. The incorporation of acetylated fiber increased the tensile modulus and reduced the impact resistance when compared to the untreated fiber reinforced polypropylene.

The composite made with the grafted polypropylene showed a notable increase in the impact resistance when compared to pure and modified polypropylene. These results point out that the dyethylmaleate modified polypropylene could be acting as a coupling agent.

Table 1. Mechanical Properties of the composites.

Material	Tensile Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Izod impact resistance (kJ/m <sup>2</sup> )
PP1 <sup>a</sup>	562 ±10	29 ±3	> 400	2.8 ±0.4
PP2-g-DEM	334 ±10	22 ±1	> 400	4.2 ±0.5
PP1 + Sisal (20%)	857 ±30	41 ±1	4.8 ±0.2	4.6 ±0.6
PP2-g-DEM + Sisal (20%)	728 ±50	40 ±1	5.5 ±0.3	5.2 ±0.6
PP1 + PP2-g-DEM + Sisal (90/10/20)	581 ±50	40 ±1	7.7 ±0.6	6.1 ±0.5
PP1 + acetylated sisal(20%)	976 ±50	41 ±1	4.2 ±0.4	3.8 ±0.4

<sup>a</sup> extruded once

## CONCLUSIONS.

The PP2-g-DEM used as third component increase the impact resistance and elongation at break of composites. However, the acetylated fiber composite showed the highest tensile modulus.

## ACKNOWLEDGEMENT

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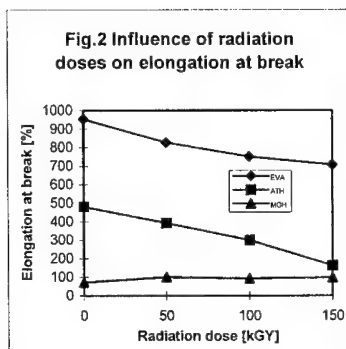
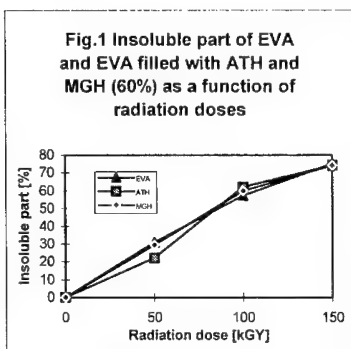
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## RADIATION CROSSLINKED EVA COPOLYMER FILLED WITH ALUMINIUM OR MAGNESIUM HYDROXIDE

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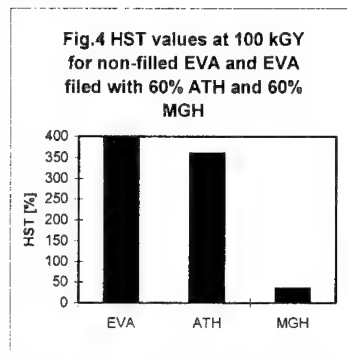
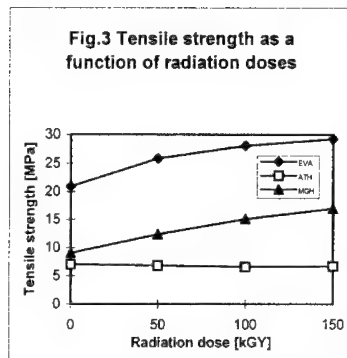
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In the case of such cable applications, where expressive insulation properties are not required, EVA copolymers can be used. EVA copolymers further enable higher filling by inorganic filler (1). Such filled compounds are difficult to crosslink by peroxides and especially by silanes because chemical reactions during processing can take place, the result of which can be not only undesirable changes of rheological properties but also lower homogeneity of crosslinking in the final product. Radiation crosslinking seems to be a promising method to solve the above problems, but in the case of EVA filled with inorganic substrates has been relatively less used so far. In this work we studied the influence of radiation doses (to 150 kGy) on EVA (MFI-7 dg/min, 27.5 wt% VA) crosslinking also in the presence of 60 wt% of aluminium hydroxide (ATH, medium particle size 0.9 - 1.3  $\mu\text{m}$ , specific surface 6-8  $\text{m}^2/\text{g}$ , surface coated) or magnesium hydroxide (MGH, 0.7-1.0  $\mu\text{m}$ , 9-11  $\text{m}^2/\text{g}$ , surface treated). Compounding prior crosslinking was carried out in the 50 ml chamber of Brabender Plasticorder at 150 °C and 50 rpm. The 1 mm thick plates were pressed at 180 °C, 2 min and then radiation crosslinked.



Insoluble part (IP) of EVA (estimated by extraction in boiling xylene) as a function of radiation doses is shown in Fig. 1. IP is independent on the filler present but it does strongly depend on radiation doses. On the other hand mechanical properties (Fig. 2, 3), namely elongation at break (EB) and tensile strength (TS) (estimated according IEC 811-1-1) of EVA generally decreased as expected without radiation due to the presence of ATH or MGH. Further comparison of both fillers (Fig. 2, 3) clearly shows the superiority of ATH as for ensuring higher EB, but just the opposite, i. e. the superiority of MGH as for ensuring higher TS, in the whole irradiation dose range. The observed effects are believed to be also in connection with inorganic substrates particle size, specific surface, surfaces treating and particle shape. Another property, important from the point of view of practical applications, is elongation at high temperature (HST, 200 °C, IEC 811-2-1). HSTs in non-filled compounds are usually in close

connection with IPs.



Higher gel content causes lower HST value. Other situation is in the presence of fillers. In spite of this aspect that gels in the presence of ATH or MGH are equal (Fig. 1) HSTs are different e.g. at 100 kGY (Fig 4). It is also obvious that HST strongly depends on the filler characteristics and that only in the case of MGH the HST value satisfies requirement according to standards (HST should be below 175%).

#### Conclusion

This study of influence of radiation crosslinking of unfilled and filled (60% ATH or MGH) EVA copolymer clearly shows:

- the insoluble fraction of EVA increases with radiation and is not influenced by the presence of fillers
- HST values are better in filled EVA in comparison with unfilled EVA, but only MGH ensures acceptable values of HST
- as for mechanical properties higher EB are achieved with ATH contrary to higher TS with MGH
- HST and mechanical properties of crosslinked filled compounds depend on filler characteristics and its interaction with polymer matrix

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#### Acknowledgement

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# PROPERTIES OF CROSSLINKED LDPE FILLED WITH MILLED GRASS

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Previously it was found that peroxide - initiated crosslinking results in a substantial improvement of strength and modulus values of LDPE filled with wood flour [1]. It was suggested that a formation of covalent bonds between the polymeric matrix and the filler surface leads to the increase of polymer - filler interactions.

In this work milled fast growing canadian grass was used as a filler in low density polyethylene. Mechanical properties of uncrosslinked composites were compared with those crosslinked either under static conditions in a press or dynamically crosslinked in a Brabender Plasticorder chamber at temperature above the decomposition temperature of the peroxide.

Finely milled grass was found to behave as an inactive filler, i.e. the increase in the filler content results in certain increase in Young's modulus accompanied with a drop in tensile strength and a large decrease in elongation at break.

The crosslinking of the matrix initiated by an organic peroxide results in a substantial increase of both modulus and tensile strength and a small improvement in elongation at break. The results indicate that the modification of the material by crosslinking leads to a formation of covalent bonds between the polymeric matrix and the filler surface resulting in an extensive increase of the adhesion on the polymer - filler interface.

The application of reactive processing, i.e. the decomposition of peroxide during the mixing of the components leads to a composite with similar mechanical properties as in the previous case, when the peroxide was mixed into the material under its decomposition temperature and the crosslinking proceeded in a press. It means that the decomposition of the peroxide under dynamic conditions results in an increased polymer - filler adhesion, similar to the material crosslinked in a press.

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# ADHESIVE PROPERTIES OF POLYPROPYLENE GRAFTED BY MALEIC ANHYDRIDE

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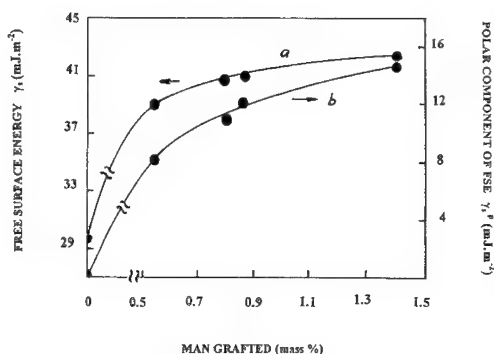
One of the method to improve the adhesive properties of iPP to polar polymers is its grafting by maleic anhydride (MAN) or by itaconic acid in quasi solid state [1-3]. It is an efficient method to increase the polarity of polypropylene. Most methods of PP grafting by MAN used previously were based on grafting in melt using butyl- and dicumyl peroxide or in solution using dibenzoyl peroxide [4].

In our case grafting of iPP by MAN was realised in quasi solid state allowed the preservation of pulverized polymer. After PP grafting by MAN the polarity of hydrophylicity was improved. In contribution the adhesive properties of grafted PP were analysed, e.g. polar component of free surface energy, total free surface energy and mechanical work of adhesion to polyvinyl acetate were evaluated.

Evaluation of free surface energy and its components was based on the measurement of compact angles with a set of testing liquids on the polymer surface. The contact angles were regularly measured in 30 s intervals and after 10 min the function  $\theta = f(t)$  was extrapolated to  $t = 0$ , where  $\theta$  is the contact angle (deg) and  $t$  is the time of wetting (s). The free surface energy and its components of the polymer were determined by the method of least squares [5].

The mechanical work of adhesion  $A_m$  ( $J.m^{-2}$ ) was determined from mechanical spectra measured by peeling of adhesive joints on dynamometer Instron.

Polar component of FSE of modified PP increased from 0.2 to 15  $mJ.m^{-2}$  and mechanical work of adhesion in adhesive joint with polyvinyl acetate increased ca 7 times in comparison with non-modified PP.



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## MODIFICATION OF POLYETHYLENE WITH ACTIVATED NATURAL ZEOLITE

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### 1. Introduction

The paper reports on the modification of high density polyethylene (HDPE) with natural activated zeolite clinoptilolite in an attempt to increase its utility properties and to improve some of its characteristics, reducing the cost of the composites at the same time.

### 2. Experiments

The material used is HDPE "Bulen" with density 0,96 g/cm<sup>3</sup> and MFI 6,73 g/10min (463K<sup>0</sup>/49,05 N). The modifier is activated natural zeolite clinoptilolite (K<sub>2</sub>Na<sub>2</sub>Ca)<sub>3</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>·23H<sub>2</sub>O with density 2,2 g/cm<sup>3</sup> and particle size 1 micron. The content of the modifier is varied in the range of 0 to 40 wt.%.

The investigated specimens with size of the working sector 60 x 9,8 x 3,8 mm have been prepared by injection molding at melt temperature 180 - 220 °C. The mechanical properties are determined by means of dynamometer TIRATEST 2115.

The calorimetric device, which measures the pressure of the gaseous products of the investigated compositions consists of a decomposition tube, connected with manometer (2,5 MPa), placed in a heating block with silicone oil. A DSC Perkin Elmer -2C Instrument is used to measure both the temperature and heat changes associated with transitions in the materials. The DSC experiments are conducted at a heating rate 10 deg/min.

### 3. Results and discussion

The structural preconditions for the interaction between clinoptilolite and the polymers are based on the special character of the surface of zeolite particles. Clinoptilolite (K<sub>2</sub>,Na<sub>2</sub>,Ca)<sub>3</sub>Al<sub>6</sub>Si<sub>30</sub>O<sub>72</sub>·23H<sub>2</sub>O is a natural aluminosilicate with a specific structure, characterized with three system channels in the particle volume. The dimensions of the polymer chain are commensurable with the dimensions of these channels in the zeolite particles, which allow the process of adsorption of the polymer chain on the zeolite surface channels. The characteristic peculiarity of zeolite, which determines its unique properties, is its ability to give off the hydrathwater without destroying the crystal lattice. The process of dehydration at 350 °C is exactly the process of zeolite filler activation. The freed volume about 30% and the sorption processes (the possibility for sorption of polymer chain on the surface channel of zeolite particle) resulting from the specific structure, determine the active modification function of dehydrated clinoptilolite. The investigated mechanical properties of filled with activated zeolite HDPE composites are shown in table 1.

Table 1

Composition, (%)	Tensile strength, MPa	Elongation, %	Modulus of elasticity, MPa	Impact strength, kJ/mm	Heat resistance, °C	Density, g/cm <sup>3</sup>	MFI, g/10min
PEHD 100 %	18,28	310,9	15215	do not break	120	0,96	6,73
PE 80%, Z 20%	20,22	24,62	19922	-	125	1,0897	4,48
PE 70% Z 30%	21,77	11,64	38797	20,42	126	1,1295	3,5
PE 60%, Z 40%	18,95	2,36	36739				

An increase of the tensile strength with the increase of zeolite content is established, and the PE composites, containing 20 and 30% dehydrated clinoptilolite, possess optimal mechanical characteristics. The increase of the modulus of elasticity by addition of mineral fillers is a logical result, and so is the decrease of the impact strength. According to the obtained results, the optimal compositions are the PE composites, containing 20% and 30% activated zeolite. Compared with the PE, these compositions show 10,7% and 19% increase of the tensile strength, acceptable elasticity and the highest values of modulus of elasticity.

It is of interest to note the density values of the PE composites. By the increase of zeolite content, they show lower density than the theoretically predicted values. The explanation should be searched in the free volume of dehydrated clinoptilolite. After dehydration at 350 °C and cooling in an atmosphere of dry air, an equilibrium saturation of the free volume with gases (mainly N<sub>2</sub>) was achieved. The desorption of N<sub>2</sub> can be achieved by exchange of water steam or by heating. The total density decrease in the experiments carried out is about 10% for the PE specimens containing 20% activated zeolite, and about 16% for the PE parts with 30% activated filler, compared with the theoretically established density values. The illustrated on Fig.1 results show the kinetics of the gas release ability of dehydrated zeolite at 200 °C, and, consequently, the activated zeolite can be considered a specific low efficient physical blowing agent.

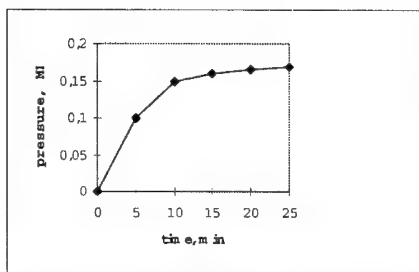


Fig.1 Pressure of the gas desorped from activated zeolite vs. heating time at 200 °C

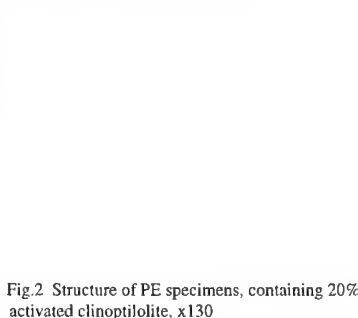


Fig.2 Structure of PE specimens, containing 20% activated clinoptilolite, x130

Activated zeolite liberates 8 - 8,5 ml/g of gases, mainly, nitrogen during the heating process. Photographs of the structure of PE specimens, containing 20% activated clinoptilolite, are shown on Fig.2. Small spherical bubbles with diameter under 0,1mm are regularly distributed in the volume of PE filled specimens.

The degree of crystallinity, estimated by DSC curves of nonisothermal melting, is 43 % for PE, and 48,2 % for the modified with 20 wt.% activated zeolite PEHD composition.

#### 4. Conclusion

The possibility for applying dehydrated natural zeolite as a modifier of PEHD is studied. The PE composites, containing 20 and 30% dehydrated activated zeolite, have optimal mechanical characteristics. These compositions show reduced density of the produced parts in comparison to the theoretically established, an increase of the tensile strength, acceptable elasticity in impact strength, and the highest values of modulus of elasticity, which means a higher suitability for production of parts with construction application.

## VISCOELASTIC AND MORPHOLOGICAL STUDY OF POLYAMIDE-6/ POLYETHYLENE/ SEBS-g-DEM TERNARY BLENDS

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### Introduction

Chemical modification of synthetic polymers during processing offers new possibilities for improving original polymer properties. One important method for the compatibilization of immiscible blends is reactive blending. Compatibilization reduces the interfacial tension between the two phases and the physical size of the domains, stabilizes the morphology and enhances the interface adhesion(1).

Blends of polyethylenes and polyamide-6 are made in order to retain the most desirable properties of both components. However, a major drawback is related to the incompatibility of such blends that can be partially overcome by adding a suitable third component. Even though these blends have been studied extensively, their viscoelastic properties at low frequencies and high temperatures have not been reported yet. Hence, in this investigation, the viscoelastic and morphological properties of ternary reactive blends of different polyethylenes, polyamide-6 and functionalized SEBS were studied.

### Experimental

A polyamide-6 (PA6), two low density polyethylenes (LDPE), a linear low density polyethylene (LLDPE) and an SEBS thermoplastic elastomer (hydrogenated terpolymer of styrene/ethylene-butylene/styrene with a styrene content of 29%) were used. The grafting of SEBS was carried out in an intermeshing corotating twin-screw extruder (Berstorff ECS2E25) at 238°C and 35 rpm. The functional monomer was diethylmaleate (DEM) and dicumyl peroxide (DCP) was used as initiator. The product was washed with acetone and methanol in order to eliminate the residual monomer. Its grafting degree was determined by FTIR spectroscopy using the characteristic bands at 1736 and 1610  $\text{cm}^{-1}$  and the method proposed by Fodor et al(2).

Ternary blends of previously dried polyamide-6/polyethylene/SEBS (either unmodified or grafted) were prepared in an intermeshing corotating twin-screw extruder (Werner & Pfleiderer ZSK 30) at 230°C and 180 rpm. The viscoelastic properties of the homopolymers and their blends were measured in the linear viscoelastic range of strain using parallel plates in a Rheometrics Dynamic Analyzer (RDA-II) at 230°C. Blend morphology was examined by SEM (Philips 505). Samples were cryogenically fractured and covered with gold/palladium. The surface of few of those was etched using toluene.

### Results and Discussion

The viscoelastic properties of the homopolymers and their blends and some morphological parameters of the blends are shown in table 1. Blends with the LLDPE and one of the LDPEs with similar viscosity were prepared at nominal shear rates where the viscosity ratio was close to unity, because the particle size achieved is the smallest(3). Michaeli's method (4) was followed in order to estimate the average strain rate in the extruder. The viscosity curves were obtained in a Capillary Rheometer at 230°C.

It can be seen from table 1 that even though the grafting degree achieved was very low (about 0.040 wt%) due to the high melt viscosity of SEBS, a lower particle size of the dispersed phase was obtained when SEBS-g-DEM was added to the blends.

Table 1. Viscoelastic properties and morphological parameters of the blends.

Material	$\eta'$ (Pa.s)	$G'$ (Pa)	VR <sup>b</sup>	Dv <sup>e</sup> (x10 <sup>6</sup> m)	Dn <sup>f</sup> (x10 <sup>6</sup> m)
PA6	90 <sup>a</sup>	<1 <sup>a</sup>	-	-	-
LDPE <sub>1</sub>	220 <sup>c</sup>	7 <sup>c</sup>	-	-	-
LDPE <sub>2</sub>	3530 <sup>c</sup>	53 <sup>c</sup>	-	-	-
LLDPE	150 <sup>c</sup>	<1 <sup>c</sup>	-	-	-
SEBS	3280 <sup>c</sup>	5080 <sup>c</sup>	-	-	-
SEBS-g-DEM	1560 <sup>c</sup>	2020 <sup>c</sup>	-	-	-
80/20, PA6/LDPE <sub>2</sub> /5 wt% SEBS-g-DEM	87 <sup>a</sup>	31 <sup>a</sup>	4.3	7	5
80/20, PA6/LDPE <sub>2</sub> /10 wt% SEBS-g-DEM	144 <sup>a</sup>	52 <sup>a</sup>	4.3	11	2
20/80, PA6/LDPE <sub>2</sub> /5 wt% SEBS-g-DEM	5680 <sup>a</sup>	435 <sup>a</sup>	0.23	4	3
80/20, PA6/LLDPE/5 wt% SEBS-g-DEM	80 <sup>a</sup>	45 <sup>a</sup>	1.3	3	1
20/80, PA6/LLDPE/5 wt% SEBS-g-DEM	400 <sup>a</sup>	240 <sup>a</sup>	0.77	1	0.4
80/20, PA6/LDPE <sub>1</sub> /5 wt% SEBS-g-DEM	80 <sup>a</sup>	48 <sup>a</sup>	1.3	7	5
20/80, PA6/LDPE <sub>1</sub> /5 wt% SEBS-g-DEM	800 <sup>a</sup>	254 <sup>a</sup>	0.77	1	0.5
80/20, PA6/LDPE <sub>1</sub> /5 wt% SEBS	160 <sup>a</sup>	72 <sup>a</sup>	1.3	11	3
20/80, PA6/LLDPE/5 wt% SEBS	150 <sup>a</sup>	50 <sup>a</sup>	1.3	16	8
20/80, PA6/LDPE <sub>1</sub> /5 wt% SEBS	3200 <sup>a</sup>	1150 <sup>a</sup>	0.77	14	5

<sup>a</sup> at 1 rad/s, <sup>b</sup> Viscosity Ratio, <sup>c</sup> at 0.1 rad/s, <sup>e</sup> and <sup>f</sup> Volume and number average particle diameter.

The stability of the phase was examined by comparison of the dispersed domain size before and after compression molding of specimens. There was almost no change of the average particle diameter (i.e. no coalescence) after molding when SEBS-g-DEM was added to the blend. Furthermore, an empty space around the dispersed phase was observed in etched specimens. This fact demonstrates that SEBS-g-DEM was located at the interface between PA6 and polyethylene.

In addition to the viscosity ratio, the influence of the elasticity on the dispersed phase size is important and should be considered(1). The viscoelasticity of the homopolymers at high temperatures is also very important when the material with a low  $G'$  is the dispersed phase. When LLDPE and LDPE with similar viscosity curves were used, a finer dispersed phase was obtained in blends with the LLDPE (LLDPE showed lower  $G'$  values).

Both  $\eta$  vs frequency and  $G'$  vs  $G''$  curves of the ternary blends with SEBS-g-DEM where polyethylene was the major component were located above the curves of the homopolymers. Additionally, when SEBS-g-DEM was incorporated into the blends where the polyolefins were the dispersed phase, the  $\eta$  vs frequency curves fell below those of similar blends with unmodified SEBS. The same blends showed higher  $G'$  values when compared to PA6 and higher  $G'$  values at low frequencies when compared to polyolefins.

#### Acknowledgement

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# CRYSTALLIZATION AND HEAT TRANSFER EFFECTS IN THE SOLIDIFICATION OF THE PP, RECYCLED HDPE AND THE BLEND OF BOTH COMPONENTS

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The main objective of this research is the simulation and modeling of heat transfer process in a non-stationary state and the development of the crystallinity in the manufacture of products based on polymers. The study of this process makes it possible the estimation of the degree of crystallinity of these compounds and, as a consequence, the determination of the usefulness of these materials, since the use of the polymers depends on their physical properties, which are strongly linked to the degree of crystallinity acquired by the sample in its solidification process<sup>1,2</sup>.

In order to evaluate the heat transfer, some experimental, isothermal and dynamic tests were carried out, by means of a Differential Scanning Calorimeter (DSC). It was also necessary to simulate several kinetic equations describing the process and expressions of the non-stationary balance of energy (including and without including the generation of energy due to the crystallization produced during the cooling). The samples analyzed were the polypropylene (PP), the recycled high density polyethylene (HDPEr) and a blend of a 70/30 PP/HDPEr.

The kinetic equations that describe the process of crystallization used in the simulation were: the expression stated by Avrami<sup>3</sup> and/or Velisaris-Seferis<sup>4</sup> to model the isothermal processes, whereas the non-isothermal processes were evaluated through the equations stated by Ozawa<sup>5</sup>, Nakamura et al.<sup>6</sup>, Kamal et al.<sup>7</sup> and Velisaris-Seferis<sup>4</sup>. The results obtained from the previous equations were compared with the experimental data in order to observe which of them was best adapted to the real process of crystallization. However, the adaptability of a kinetic model of crystallization to isothermal as well as dynamic processes will mainly depend on the values previously obtained in the kinetic parameters. These parameters are specific to each polymer or compound.

In the case of the studied polymers, the equations that model the kinetics of the isothermal crystallization are, in general, well adapted to the experimental profile. There is just a little discrepancy in some crystallization temperatures of the blend. This difference could be attributed to the fact that at the moment of occurring the crystallization, one of the components impedes the crystallization of the other, producing a little displacement in the curve of experimental cooling. As far as the modeling of non-isothermal processes is concerned, the equation best adapted to the experimental data was the one developed by Velisaris-Seferis (figure 1).

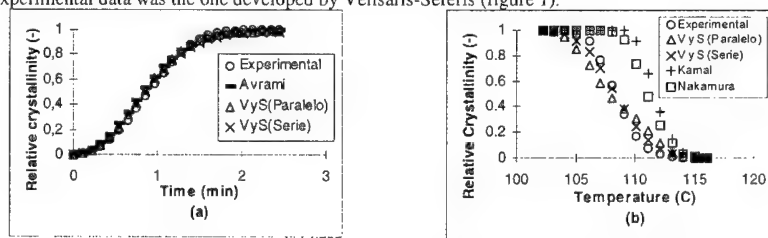


Figure 1.- Development of Relative Crystallinity of PP: (a) For Isothermal Crystallization (117 °C).  
(b) For non-Isothermal Crystallization (15 °C/min.)

One of the assumptions that were taken into account for the elaboration of the balance, was that the sample took the form of a plaque with a determined thickness whereas the other dimensions present an infinite length. Therefore, by solidifying a sample, through an isothermal or dynamic method, each of the points placed along the coordinate that is perpendicular to the plane of the plaque becomes cool at a certain speed. When the cooling is isothermal, the surfaces of the plaque present a constant temperature whereas the internal points change from the initial temperature to the cooling temperature (figure 2a). Due to the fact that the temperature of the different points varies with time, the crystallization process is dynamic. All these facts lead to think that the kinetics of crystallization of the different points through the thickness must be evaluated through a non-isothermal equation. However, depending on the thickness and on the thermal diffusiveness of the material under discussion, sometimes the kinetics could be evaluated through an isothermal equation.

From the results obtained, the research found that in the case of the studied polymers, the temperature profiles (isothermal and non-isothermal) overlap, including and without including the term of energy generation. This means that the process of crystallization provides the system a negligible degree of energy. As far as the isothermal crystallization is concerned, the experiment showed that as the cooling temperature increases, there is a decrease in the range of crystallization. Therefore, the crystallization reached by the polymers is increasingly lower, since there is less time for the formation and organization of the crystals. At the same time, the profiles of crystallinity obtained increase from the surface to the center of the material, and have the shape of a plateau.

With respect to the non-isothermal crystallization, the crystallinity profile is flat, due to the similarity of the thermal history experienced by each of the points along the thickness, because the speeds of cooling analyzed in this research were low enough for the studied polymers. As a consequence, their corresponding temperature profiles become parallel (figure 2b). This shows that after the initial transition period, each point inside the plaque cools down at the same speed and the heat flow from the polymer to the environments becomes a constant. On the other hand, as the cooling speed increases the transition period is higher. All these facts depend on the thermal diffusiveness of the material; the higher is the value, more uniform is the temperature profile along the thickness.

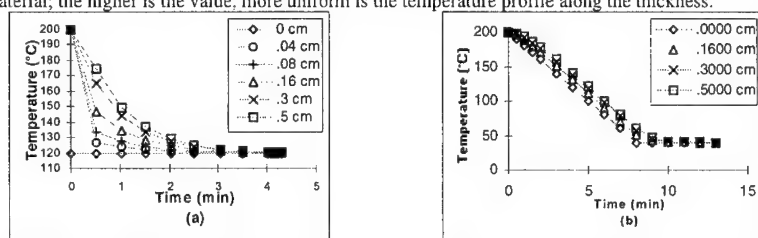


Figure 2.- Temperature Variation with time of HDPEr, at different locating within the plaque: (a) For Isothermal Crystallization (120 °C). (b) For non-Isothermal Crystallization (20 °C/min.).

In conclusion, the study of the heat transfer in the manufacture of plastic material, makes it possible to estimate the degree of crystallinity of those compounds. Therefore, it is possible to foresee the usefulness of those materials because the use of the polymers is strongly linked to the degree of crystallinity acquired by the sample during the solidification process.

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## ELECTROCHROMISM OF THE COMPOSITE FILM OF ETHYLENE-VINYL ALCOHOL COPOLYMER AND POLYPYRROLE

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### INTRODUCTION

Conducting polymers are attractive materials for optical control and display devices because of the electrochromism associated with the redox process of the polymer. Among a variety of materials that exhibit electrochromism, polypyrrole is one of the promising materials for electrochromic display because polypyrrole can be reversibly switched between oxidized (conducting) and the reduced (insulating) states [1]. However, polypyrrole is not necessarily a suitable material in the practical application due to a short life cycle time and poor mechanical properties. Here we report the improvement of cycle life time by use of the composite film of ethylene-vinyl alcohol copolymer (EVOH) and polypyrrole (PPy).

### EXPERIMENTAL

The electrochemical polymerization was carried out at a constant current density ( $0.15 \text{ mA}\cdot\text{cm}^{-2}$ ) and temperature ( $20^\circ\text{C}$ ) using a solution containing ethanol,  $0.1 \text{ M}$  pyrrole and  $0.1 \text{ M}$  lithium perchlorate in a cell comprising two electrodes. Indium-tin oxide on which EVOH containing lithium perchlorate was coated, and platinum were used, respectively, as anode and cathode. The change in UV/VIS spectra of the EVOH-PPy composite film coated on the ITO glass by the repeated application of potentials ( $\pm 1.0 \text{ V}$ ,  $10 \text{ s}$ ) was measured in ethanol containing lithium perchlorate. Also, cyclic voltammetry of the composite film was measured.

### RESULTS AND DISCUSSIONS

The change in UV/VIS spectra of the EVOH-PPy composite film between the application of  $+1.0 \text{ V}$  and  $-1.0 \text{ V}$  with cycle number of the redox process was shown in FIG. 1. The absorptions at  $800\text{-}900 \text{ nm}$  and  $300\text{-}400 \text{ nm}$  pertain to the oxidized and reduced PPy, respectively. When the potential was varied from  $-1.0 \text{ V}$  to  $+1.0 \text{ V}$ , the absorbance at  $300\text{-}400 \text{ nm}$  decreased, whereas the value at  $800\text{-}900 \text{ nm}$  increased at 100 cycles. The color of the film reversibly changed from yellow to brown. However, as the cycle number increased, the change of the absorbance gradually became small, and at 10000 cycles absorption peak pattern became not to change.

The difference of absorbance at  $800 \text{ nm}$  between the application of  $+1.0 \text{ V}$  and

-1.0 V ( $\Delta A$ ) versus cycle number of the redox process was shown in FIG. 2. In the PPy film,  $\Delta A$  rapidly decreased at ca. 100 cycles and the color of the film became not to change. On the contrary,  $\Delta A$  almost did not change until ca. 7000 cycles in the composite film. Also, the same tendency was observed in the relation of elementary electric charge and cycle number of the redox process in the films measured by cyclic voltammetry. These results indicate that the durability by the repeated application of potentials markedly improved in the composite film.

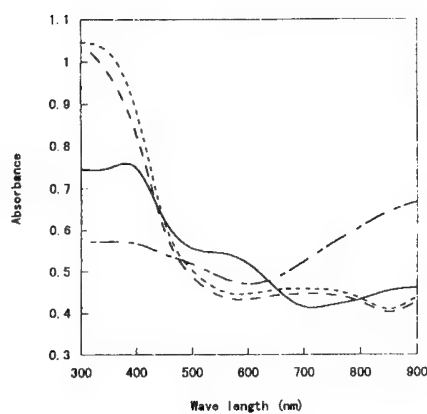


FIG. 1. Change in UV/VIS spectra of the EVOH-PPy composite film between the application of +1.0 V and -1.0 V with cycle number of the redox process.

(—) -1.0 V, 100 cycles,  
 (---) +1.0 V, 100 cycles,  
 (- · -) -1.0 V, 10000 cycles,  
 (· · ·) +1.0 V, 10000 cycles

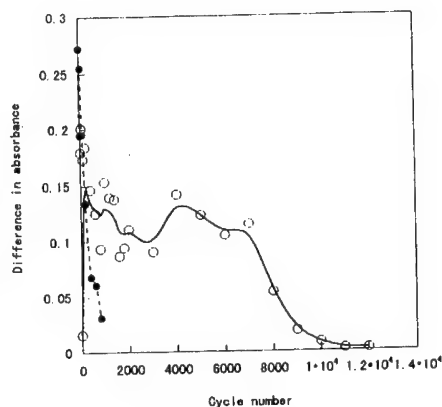


FIG. 2. Difference in absorbance at 800 nm between the application of +1.0 V and -1.0 V versus cycle number of the redox process for the EVOH/PPy and PPy films.

(— o —) EVOH / PPy film,  
 (— • —) PPy film

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## HEAT AND CHEMICAL AGING OF MODIFIED GLASS-REINFORCED POLYPROPYLENE

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A great advance in the area of polyolefine composites has been made in the last decades. Chemical modification of polyolefines, chemical binding of a polymer and a filler for example, may endow composites with a complex of unique properties. Modification of the polymers (polypropylene in particular) by grafting of reactive functionalities at synthesis or compounding is a necessary condition for creation of high-strength polyolefine composites, containing glass fiber or other reinforcer [1]. The conception of the said modification consists in creation of chemical adhesion on a polymer/filler interface [2]. Unfortunately, chemical modification, such as generation of carboxylic or imide groups in macromolecules, results in noticeable decreasing of polypropylene thermostability: oxidation of the polymer proceeds practically without induction period. Thermostabilization of modified polyolefine composites is complicated by possible interaction between an antioxidant and grafted reactive groups of macromolecules. This interaction diminishes polymer-filler chemical adhesion.

In the present study the comparative behavior of modified and unmodified glass-reinforced polypropylene during aging in air (135°C) and in antifreeze (115°C) have been investigated. The approaches to thermostabilization of the composites were proposed. Mechanical properties (tensile strength, flexural strength, impact strength) and melt flow were measured for initial and aged samples. According to Hg-porosimetry data, unmodified composite has macroporous structure (maximal pores size 30010 Å); phases separation increases in the course of aging. On the contrary, initial modified composite is characterized by dense structure, maximal pores size is 710 Å. Aging results in the structure compaction; pores size diminishes. The unmodified composite displays a significant failure of mechanical properties already after 10 days of heat aging; chemical aging provides a slight increasing of impact strength of the samples because of plasticization by antifreeze. By DSC and O<sub>2</sub>-uptake results, stabilized modified composite has high thermooxidative stability. This glass-reinforced polypropylene holds its molecular weight characteristics during aging in air and antifreeze.

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## PARTIAL CROSSLINKING OF HETEROPHASIC ETHYLENE - PROPYLENE COPOLYMER

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Chemical modification of polyolefins can be performed as the solution, melt and solid phase reaction. Mostly the modification reactions in the solution and in the melt have been studied. Commonly these reactions have the radical character [1]. Radical modification of PP at higher temperatures (in the melt) leads to its strong degradation typically [2]. The excess of the degradation reaction is lower by the modification in the solid phase [3], but mostly the grafting of polyolefins in solid phase has been reported [4,5].

This report is dealing with the radical modification of the heterophasic ethylene-propylene copolymer with the peroxide and without the crosslinking agent. This copolymer consists of the PP matrix and the dispersed EPR phase.

By the reaction of this copolymer with the peroxide in the melt and also in the solid phase, it comes to the degradation of the PP matrix and to the partial crosslinking of EPR particles. The degree of the degradation/crosslinking depends on the type of the initiator and the temperature. Due to crosslinking of the EPR phase, the EPR-peak in the dynamic - mechanical spectrum shifts towards higher temperatures. The modification with the peroxide in the solid phase leads to the formation of inhomogeneities in the modified copolymer.

By the reaction with the peroxide and the crosslinking agent in the solid phase, larger inhomogeneities are built than in the case of the reaction only with the peroxide. Probably it comes to the building of the network-like structure of the crosslinked EPR particles in the degraded PP matrix. Further extrusion of the solid phase modified copolymer destroys this structure. As a result the melt flow index of the copolymer is increased (table 1).

The reaction of the copolymer with the peroxide and the crosslinking agent in the melt has been also investigated. In this case no evident inhomogeneities are formed. Modified copolymer has higher E-modulus and lower impact strength at -20°C (tested on unnotched specimens).

*Table 1: Variation of the melt flow index of the heterophasic ethylene-propylene copolymer with 12 wt.% EPR (KSC..12) modified in the solid phase with peroxide and crosslinking agent after the pelletization*

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Sample	c(TBPB) [pph]	c(CROS) [pph]	MFI (Powder) [g/10min]	MFI (Pellet) [g/10min]	MFI (Powder)/ MFI (Pellet)
KSC..12	-	-	7.2	7.7	1.1
1	0.25	0.19	5.8	21.2	3.6
2	0.25	0.38	0.74	13.5	18.2
3	0.5	0.38	2.6	23.7	8.9

CROS = crosslinking agent

KSC..12 = heterophasic ethylene-propylene copolymer with 12%wt. EPR, product of PCD Polymere Ltd.

TBPB = tert-butyl-peroxybenzoate

MFI = melt flow index by 230°C and 2.16 kg

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## EVALUATION OF THE MORPHOLOGICAL STRUCTURE OF POLYMERS

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The morphological structure of polymers on a certain quantitative and qualitative level expresses a development stage of the preparation of polymer material (fibers, sheets) with given physical properties. Polymer materials on a lower development technological stage of preparation (non oriented fibres contain structural configurations of crystallites in a polymer amorphous phase -spherulites). Spherulites are three dimensional morphological configurations with a certain size and periodicity, attaining the dimensions comparable with the wave length of visible light. They have various size and shape. A non deformed spherulite is symmetric and it has properties of an isotropic polymer. A deformed spherulite demonstrates itself as an isotropic configuration of crystalline grouping in an isotropic environment.

With regard to the optical dimensions of the morphological configurations optical methods are used to evaluate the morphological structure (light polarization microscope, electron microscope, X-ray methods ...). The small angle scattering of the polarized laser beam SALS suitably supplements the former mentioned methods at the study of the morphological structure of polymers. The laser with incident light on spherulite in polymer material is scattered with a small angle and the diffusion is registered in the background. The scattered image renders more informations on the morphological structure of the studied material (kind of the structural configuration, size, deformation degree).

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**P-43**

**MODIFICATION OF POLYETHYLENE WITH ORGANIC AND  
INORGANIC FILLERS**

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Polyolefines are used in a wide range, especially in manufacturing of films and sidetrip containers what leads to manage these appeared waste. On account of specific properties of the packing materials (sterility) the after-usage recyclates from these materials can not be used in the production of packages, but it is possible theirs usage in a technical application.

In our previous papers [ 1 - 3 ] we have described the advantages of physical modification of polyethylene recyclate with recyclates from multilayer films waste or inorganic filler.

In this paper we report the effect of physical modification of HDPE or polyethylene recyclate with PA/PE recyclate, PUR recyclates and fly ash as a filler on mechanical, rheological, thermal and electrical properties of the polymer blends and composites.

The polymer blends and composites were prepared by extrusion moulding on a single-screw extruder with using a proper mixing head.

The basic physical, thermal and electrical properties of the polymer blends and composites were tested according to ISO norm. The component distribution in the polymer matrix was determined by microscopic measurements by scanning electron microscopy.

## RESULTS

The influence of components content on the processing, mechanical, thermal and electrical properties of the polymer blends of polyethylene and PA/PE recyclate was determined. Results of examinations are summarized in table 1.

Table 1. The influence of polyethylene content on a properties of blends PA/PE

PE content, wt %	0	10	25	35	50	60	75	100
Tensile strength, MPa	13,1	13,3	15,0	16,1	17,2	16,5	16,2	12,5
Hardness HB, MPa	13,1	13,0	12,5	12,3	12,2	11,5	11,3	10,8
Resistivity, kV/mm	30,2	31,3	32,3	33,3	36,4	39,4	41,3	43,7
Electric arc resistance EAR,S	140	150	153	158	160	164	170	175

The performed examination shown that properties of blends of PE recyclate modified by PA/PE recyclate are considerably improved in comparison with pure recyclate. An increasing of composite hardness can be obtain by modification of composite by PUR crumb an fly ash as a filler. Positive effect of modification is improving of electrical properties what allow to extend a range of composite usage in the future.

## CONCLUSIONS

Properties of the polymer blends and composite materials allow to think that it can be used in different products. The essential advantage is using the waste material in the blends and composite what leads to decreasing of resulting waste. The obtain composite by a physical modification of polyethylene recyclate should have better tensile strength, thermal and electrical properties.

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## **BLENDED POLYPROPYLENE FIBRES**

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Polypropylene (PP) as a hydrophobic polymer has a little capability to fix polar molecules. Owing to this fact we have 3 possibilities of dyeing of PP fibres:

A. The dyeing of unmodified PP with pigments during the preparation of fibres [1-3].

B. The preparation of dyed master batch (consisting of functional additive and the dyestuff and its incorporation into PP essentially before the spinning [4-7].

C. The modification of PP with additive(s), its spinning and dyeing the modified PP fibres with dyestuff by exhaustion method [8-10].

The polar molecules of dyestuffs are fixed either by polar groups of the additive or by groups of modified PP. Modification of PP can be made chemically or physically. Each of mentioned methods has its own advantages.

According to the results of our work the physical modification of PP (i.e. the preparation of blended M/F fibres PP + additive fixing the dyestuff and the dyeing of the modified PP fibres by exhaustion method) is an effective way to prepare the dyed PP fibres. Closed, uniforme internal structure of PP fibres is changed by additive and it is more accessible for smaller molecules of dyestuff. The blended fibres are effectively dyeable if an additive contains in addition groups capable to fix the dyestuff.

The other effective way is the method described as B.

The topic of presented paper was the preparation of experimental blended PP fibres from mixtures PP + terpolymer acrylonitrile-butadiene-styrene (ABS, the content 0 - 40 wt.%) and PP + polystyrene (PS, the content 0 - 25 wt. %) and the study of their properties, essentially the dyeability.

The spinning process was stable in all interval of compositions, the process of drawing showed that the polystyrene is less suitable in comparison with terpolymer ABS.

Some mechanical properties and the dyeability of blended PP fibres were determined as a dependance of the type and the amount of additive, type of the disperse dyestuff and drawing ratio. We observed that the tenacity drops and elongation to break is not practically influenced.

The dyeability of blended PP fibres rises with the amount of additive. More in the case when ABS was used. The type of disperse dyestuff has an important role. on the contrary the drawing ratio has a little influence.

The dyeability (as an amount of fixed dyestuff in mg in 1 g of dyed PP fibres after the washing) is given in the table.

Table Dyeability of PP fibres modified by ABS and PS

Content of additive, wt. %		Content of fixed dye, mg of dyestuff/1 g of dyed fibre			
		C.I. Disperse Red 60		C.I. Disperse Blue 3	
ABS	PS	$\lambda = 3$	$\lambda = 3.5$	$\lambda = 3$	$\lambda = 3.5$
0	0	0.2	0.17	0.2	0.2
5	0	0.93	1.1	0.7	1.0
10	0	2.37	2.27	1.2	1.53
15	0	3.07	3.1	1.73	1.6
20	0	3.57	3.63	2.37	2.13
25	0	4.7	4.43	2.6	2.23
30	0	5.8	6.17	2.7	2.63
40	0	6.1	6.47	3.06	2.93
0	5	0.33	0.53	0.4	0.43
0	10	1.0	1.03	0.57	0.63
0	15	1.5	1.1	0.9	0.97
0	20	2.3	-	1.1	-
0	25	2.47	-	1.23	-

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**BROMINATED POLYETHYLENE.  
SYNTHESIS AND USE AS INTERMEDIATE FOR THE PREPARATION  
OF NEW POLYMERIC STABILISERS**

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Hindered amine stabilisers (HAS) specially 2,2,6,6 - tetramethylpiperidine derivatives are well known protecting agents against light and thermal oxidation of polymers<sup>1,2</sup>. To eliminate volatility of HAS from the protected polymer at processing or in common use, the polymeric or oligomeric HAS are used. To obtain good protection of polymer, the stabiliser should be homogeneously distributed in protected polymer<sup>2,3</sup>. In ideal case, the stabiliser is well soluble in protected polymer. However there are only limited examples of mutual solubility of polymers. Chlorinated polyethylenes belong to such polymers. It is the reason that they are frequently used to increase tensile strength of PVC<sup>4</sup>, as compatibilisers<sup>5</sup> and form the transparent mixtures with many polymers. Similar properties is possible to expect for brominated polyethylene too. Therefore brominated polyethylene seems to be a good candidate for binding of stabilisers, and to achieve good miscibility with protected polymer and therefore also good protecting activity. Advantage of brominated polymers is easier substitution of bromine in comparison with chlorine, to connect active structures. Moreover, bromine can decrease the flammability of the resulting polymer mixture.

In the present work we try to combine the advantages of good stabilising properties of HAS with the good miscibility of brominated polyethylene to achieve optimal stabilising efficiency. Therefore the completely hydrobrominated polycyclooctene (brominated polyethylene) was prepared. Different HAS derivatives were used for substitution of bromine. For example partial substitution of the bromine of the completely hydrobrominated polycyclooctene with 4 - amino - 2,2,6,6 - tetramethylpiperidin leads to bounding of 4 - amino - 2,2,6,6 -

tetramethylpiperidin to polymer. Resulting polymer (HAS I) according  $^1\text{H}$  NMR analysis contains 42 mol % of substituted 4 - aminoyl - 2,2,6,6 - tetramethylpiperidine groups, 53 mol % of unsubstituted hydrobrominated structure unites and 5 mol % of unsaturated structural unites coming from elimination reaction.

To test the efficiency of these new polymeric stabilizers they were included in an EPDM and polycyclooctene matrix. Both thermal (80 °C) and photoaging were evaluated by measuring the carbonyl absorption for stabilized and unstabilized polymers.

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## RECYCLING OF POLYOLEFINS, PART II: BLENDS OF SEVERAL POLYMERS

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The most used plastics, specifically in packing and wrapping, are polyolefins (PP, HDPE, LDPE, etc.). These polymers represent about 70% of the plastics used. Because of this high percentage, that is visible in the wastes, and consequently provokes environmental problems. The aim of the present paper is to study the feasibility of recycling of polyolefins with some additives as copolymers in order to improve the mechanical properties and increase the useful life of the blends. In order to develop this goal, several blends were mixed: a) PP with a recycled polyolefins (POD), formed by 23% of PP, 45% of HDPE and 32% of LDPE and b) LDPE with the POD.

### a) PP/POD

In table 1, the temperatures of the thermograms made to PP with POD blends are shown. As you observe, the fusion temperatures of the phases do not change considerably and the fusion endotherms registered belong to the PP and polyethylenes phases. These results show a cocrystallization of the PE and also indicate the presence of poor interaction among the phases. On the other hand, there is a decrease of the fusion heat. This effect is deeper at a 50% concentration of POD. The polyblend of PP/POD present a synergism in the Young module (table 1) for a 90% composition of PP, behaving in an additive form for the rest of the compositions. This is probably due to the change of morphology presented.

Material	Thermal Properties			Mechanical Properties			
	Temp. 1 (°C)	Temp. 2 (°C)	$\Delta H_f$ (J/g)	E (Kg/mm <sup>2</sup> )	UTS (Kg/mm <sup>2</sup> )	$\epsilon_B$ (%)	IS (J/m)
PP (%)							
100	-----	161.62	88.64	96.55	3.95	16.54	15.45
90	126.30	160.69	75.22	110.43	3.63	10.08	12.81
80	126.17	160.75	77.92	93.6	3.65	7.58	12.00
70	125.40	159.28	77.57	98.17	3.57	8.19	9.91
60	125.70	159.79	77.46	85.73	3.19	6.71	7.92
50	128.16	159.40	65.24	77.41	2.66	5.43	7.25
0	127.98	160.13	106.26	46.26	2.83	11.53	10.49

Table 1: Variation of the mechanical and thermal properties of the PP with POD (Temp. temperature,  $\Delta H_f$ : fusion heat, E: Young's Modulus, UTS: Ultimate tensile strength,  $\epsilon_B$ : Elongation at break, IS: Impact Strength).

The fact that the fusion temperatures found for the blend do not change with the composition shows that the increase of the Young module is only due to morphological causes. The elongation to rupture and the resistance to impact (table 1) are the properties more affected by the PP/POD blend. It behaves similarly to the binary blends of polyolefins.

With the purpose of improving the mechanical properties of the PP/POD blend, a random copolymer of propylene-ethylene was added. The copolymer had a 97% composition of propylene and a 3% of

ethylene. The composition chosen to be compatibilized, is 80% of PP and 20% of POD, because at this composition the properties of the blend present a similar value to the one obtained by pure PP. On the other hand, at this proportion, the composition contains the greatest possible amount of recycling material.

In order to assess the effect of the addition of the compatibilizant agent to the PP/POD blend (80/20), a copolymer was added to different compositions varying between 5 and 20% in weight. From the mechanical tests, one can conclude that the optimal concentration of the compatibilizant agent is 12%, because at this composition the elongation to rupture and the resistance to impact is improved, without greatly affecting the rigidity. On the other hand, the morphology of the blends obtained by SEM (fig. 2) confirm the fact that the disperse phase POD is more embedded in the matrix phase of PP when it is compatibilized, besides presenting a slightly smaller size of the particle, giving rise to a decrease of the interfacial tension.

As a result, one can conclude that it is possible to recycle the POD up to 20% with PP. This implies a decrease in the cost of raw materials. The addition of a copolymer to the 12% composition improves the interfacial adhesion.

#### b) LDPE/POD

Table 2 shows the results obtained by the mechanical and thermal behavior of the LDPE/POD blends. The Young's Module and strength at break show an additive behavior. In thermal studies of the blends carried out, one can observe that at concentration of 80 and 90% of the LDPE, there are four crystalline phases. As a result there are four fusion temperature. For the rest of the compositions there were three peaks corresponding to the phases of PP, LDPE and the cocrystalline phases of the LDPE-HDPE. This is an evidence that there is a shift in the fusion temperature(Temp.2), since there is an increase in the concentration of HDPE in the blends. The values obtained by the elongation at break and the impact strength for this blend, reflect the incompatibility between the phases of PP, and PE.

Material LDPE (%)	Thermal Properties					Mechanical Properties			
	Temp.1 (°C)	Temp.2 (°C)	Temp.3 (°C)	Temp.4 (°C)	$\Delta H_f$ (J/g)	E Kg/mm <sup>2</sup>	$\sigma_B$ Kg/mm <sup>2</sup>	$\epsilon_B$ (%)	IS (J/m)
100	110.7	-----	-----	-----	77.3	13.0	0.7	98.0	166.0
90	109	117	123	162	96.0	11.0	0.5	84.7	74.4
80	109	119	124	162	97.0	20.0	0.9	50.2	22.9
70	110	-----	124	163	91.0	25.9	1.0	57.4	20.4
60	109	-----	125	162	92.0	27.2	1.8	20.3	20.2
50	109	-----	127	162	100.0	30.4	1.9	20.2	13.7
0	-----	-----	128	160	106.0	45.9	2.8	12.1	14.0

Table 2: Variation of the Mechanical and thermal properties of the LDPE with POD.

( T.: Temperature,  $\Delta H_f$ : fusion heat, E: Young's Modulus, UTS: Ultimate tensile strength,  $\epsilon_B$ : elongation at break, IS: Impact Strength)

A composition of 10% of POD with LDPE was selected and a copolymer at random was added. Young's modulus increases with the addition of small quantities of compatibilizer. The elongation at break and the impact strength suffer a greater deterioration at lower concentrations of the compatibilizer. These properties show that the material becomes rigid, losing ductility. One could infer that you want to increase the rigidity of the blends, the optimal concentration would be of 10%. However, if it is not the main goal, the appropriate measure is not to add this copolymer.

# THE EFFECT OF MATRIX-FILLER INTERACTIONS ON THERMAL CAPACITY OF LOW-DENSITY POLYETHYLENE/GRAPHITE COMPOSITE

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Thermal capacities ( $C_v$ ) of low density polyethylene (LDPE) filled with graphite have been measured in a broad range of the filler concentration. A significant deviation from the additive rule

$$C_v = C_{vf} w_f + C_{vm} w_m$$

( $w$  being the weight portion of the component, subscript  $f$  and  $m$  is for filler and matrix, respectively) was observed. Since thermal capacity at constant volume is directly related to the internal energy of system ( $U$ )

$$C_v = (dU / dT)_v,$$

the deviation observed can be attributed to the matrix - filler interaction, such as a formation of the interphase. It is supposed that the thermal capacity of the interphase differs from the  $C_v$  of the bulk polymer as a result of a decrease of the number of the rotational degree of freedom.

The experimental dependence was described by an equation

$$C_{v,c} = (C_{vm} - c w_f^n) (1 - w_f) + C_{vf} w_f$$

and a good fit with the experimental data was obtained. The parameter  $n$  is characterized by the ratio of the interphase formed to the total filler content

$$w_i \approx w_f^n$$

and the  $c$  is related to the difference between the capacity of the polymer in the absence of the filler and the capacity of the interphase in the limited case when the whole polymer is bound to the filler surface.

The data obtained from the capacity dependence on the filler content are compared with other physical data.

**SPECTRAL CHARACTERISTICS OF MULTIFUNCTIONAL PROBES  
BASED ON PYRENE IN SOLUTION AND IN POLYMER MATRIX**

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Spectral properties of multifunctional probes derived from 4-(1-pyrene)butyric acid and 2,2,6,6-tetramethyl-4-hydroxypiperidine in solution and in polymer matrices were investigated. In absorption spectra the well resolved absorption of pyrene dominates which is little influenced by the medium. The absorption of the hydrochloride derived from the amine in nonpolar matrix is rather diffuse. All fluorescence probes with different functional groups at sterically hindered center yield well resolved emission spectrum which was the same in solution and in polymer matrix at low concentration. The main features of the emission spectrum were not influenced by the polarity of the medium. The red shifted excimer emission was observed for hydrochloride at the concentrations in the solution ( $10^{-3} \text{ mol.dm}^{-3}$ ) and in the solid matrix ( $0.1 \text{ mol.kg}^{-1}$ ), at which the parent probe yields monomer emission only, what indicates the formation of ground state aggregates. Steady state and lifetime measurements indicate that the emission of N-oxyl type probe is quenched by about 50 % not depending on the medium. This new radiationless channel in N-oxyl type probe is comparable with the rate of radiation channel.



# INVESTIGATIONS OF MACROMOLECULAR STRUCTURES OF MODIFIED POLYOLEFINS BY OPTICAL AND HYDRODYNAMIC METHODS

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The investigations of the architecture of macromolecules and their chains rigidity and conformation are an essential prerequisite for obtaining modified polyolefins for advanced polymeric materials.

Flow birefringence (FB) is one of the most effective methods for obtaining this information. The optical anisotropy of molecules is the tensor which is formed from the optical anisotropy of their components. Therefore, FB is very useful for establishing the arrangement of copolymer components, whereas most other methods determine only the relative quantity of these components.

The sign of FB is a very sensitive indicator of macromolecular architecture. In copolymers of propylene with styrene the benzene rings provide the major contribution to the optical anisotropy of the macromolecule. The optical anisotropy of a block copolymer has to be the additive sum of the optical anisotropy of parent homopolymers, in the first approximation. For a graft copolymer with polystyrene side chains, optical anisotropy must be positive. The values of optical anisotropy of the Kuhn segment  $\Delta\alpha$  of investigated homopolymers and copolymers are presented in the Table:

POLYMER	SOLVENT	% OF STYRENE	$\Delta\alpha \text{ \AA}^3$
Polystyrene	Bromoform	100	-23.7
Atactic	Benzene	0	+ 8.8
Polypropylene			
Copolymer obtained by chemical modifications	Clorobenzene	70	+ 3.5
Copolymer obtained by mechanochemical modification	Clorobenzene	36	- 1.5

The copolymers were obtained at the Polymer Institute of the Slovak Academy of Sciences by chemical or mechanochemical modification of atactic polypropylene. The additivity rule gives  $\Delta\alpha = -2.9 \text{ \AA}^3$  for the last copolymer, which is close to the experimental value of  $\Delta\alpha$ . This means that polystyrene components are located in the main chain, and this copolymer has the block architecture. The additivity rule does not give the positive  $\Delta\alpha$  value for the first copolymer in contrast with the experiment. Accordingly this copolymer has the graft structure. The comparison with the values of  $\Delta\alpha$  and intrinsic viscosity for model graft copolymers shows that the molecules of this copolymer have long widely spaced side polystyrene chains.

Moreover, FB allows the determination of the rigidity and conformation of side chains. Polyalkylstyrenes were studied. Side polyethylene chains of these comblike macromolecules may be regarded as wormlike chains the first link of which is rigidly bonded to the polystyrene main chain and forms an angle of  $90^\circ$  with it. In this case the side chain optical anisotropy in the coordinates system of its first element  $\Delta b$  is

$$\Delta b = (\Delta\alpha - \Delta a)/(-1/2)S,$$

where  $(\Delta\alpha - \Delta a)$  is the difference between the experimental optical anisotropy values of the copolymer and that of polystyrene and  $S$  is the number of side chains in the Kuhn segment.

The  $\Delta b$  value was calculated versus the number of carbon atoms  $m$  in polyethylene for two models: 1) a usual polyethylene chain and 2) a completely extended polyethylene macromolecule without bond angle deformations. The experimental  $\Delta b$  values for  $m=6$  (polyhexylstyrene) and  $m=10$  (polydecylstyrene) exclude the rodlike conformation of side chains.

Two other proofs of the coil conformations (low rigidity) of side chains were obtained: 1) the hydrodynamic diameter of the macromolecule is  $5 \text{ \AA}$  for polystyrene and that of polydecylstyrene is only  $7 \text{ \AA}$  2) the splitting of the  $820 \text{ cm}^{-1}$  band in the IR spectra of polydecylstyrene and its monomer shows that the polyethylene "tail" can approach the benzene ring.

In contrast, in all other comblike poly- $\alpha$ -olefines, poly(alkylacrylate)s, and poly(alkyl methacrylate)s the interaction between side chains leads to a great increase in their rigidity and orientational order (rodlike conformation).

In our opinion the strong specific interactions between the benzene ring and the two first side chain links in polyalkylstyrene lead to the splitting off one of hydrogen atoms of some methyl in the cases when  $m=1,2$  and to much weaker interactions between long side chains. These results of interactions profoundly affect the solubility and utility of polymers. Polymethylstyrene and polyethylstyrene consist of inter- and intramolecularly crosslinked molecules in almost equal quantities. The former give an insoluble gel. The latter are well dissolved, but  $\Theta$ - solutions have the M-K-H exponents  $a=0.2+0.3$ . Polyalkylstyrenes with  $m=5, 6$ , and  $10$  can be dissolved in many solvents. These solutions have usual values  $a \geq 0.5$ .

Polyalkylstyrenes were obtained and investigated at the Institute of Macromolecular Compounds of Russian Academy of Sciences. New thermostable and optically transparent glues were developed on their basis. Side chains high mobility leads to low glass transition temperature of polymers and the presence of benzene rings makes it possible to raise their refractive index to that of inorganic glass. This made it possible to select the compositions of random copolymers of alkylstyrenes and alkylacrylates, which exhibit transparency, high elasticity, and frost resistance. They are utilized for complex optical articles.

**STABILITY ANALYSIS OF NEWTONIAN-PTT COEXTRUSION FIBER SPINNING**

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Linear stability analysis has been applied to a coextrusion fiber spinning flow that consists of a Newtonian fluid as a core-layer and a Phan-Thien/Tanner (PTT) fluid as a skin-layer. These two chosen fluids show completely different rheological behaviors. The stability of this coextrusion system was influenced by the choice of three characteristic parameters: the skin layer fraction, the extensional parameter and the shear thinning parameter in Phan-Thien/Tanner model. The linear stability results point that the viscoelastic skin layer (PTT fluid) has a stabilizing effect that delays the beginning of draw resonance. Under fixed composition, the stability envelopes changed from upturned curves to flattened ones as extensional force dominated the system. The neutral stable curves closed to the horizontal line at a critical draw ratio of around 20, showing similar behavior to Newtonian fluids when shear thinning effects dominate the system or it has a very high Deborah number.

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**EFFECT OF STYRENE-BUTADIENE-STYRENE BLOCK COPOLYMER ON  
DYNAMIC-MECHANICAL PROPERTIES OF HIGH-IMPACT POLYSTYRENE**

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For the selection of the polymer materials and polymer blends for various fields of applications, dynamic-mechanical properties, the primary viscoelastic functions as well as the stability of materials on different loads are very important. Since polymer materials are viscoelastic, their mechanical properties are dependent on temperature and time. The dynamic-mechanical properties of high-impact polystyrene, (PS-HI) and blends of PS-HI and styrene-butadiene-styrene block copolymer, (SBS) were investigated. In the conditions of dynamic-mechanical load, the investigated systems will have different behaviours due to the various content of the hard phase, polystyrene and soft phase, polybutadiene. The investigations were done by DMA analysis. The primary viscoelastic functions were determined. The influence of the constant stress on the strain and moduls at various temperatures was examined. The effects of the time on moduls changes was obtained by generated the master curves. The viscoelastic functions and the stability on the constant load, the changes on the moduls with time and temperature depend on the amount of polystyrene in examined copolymers and blends. This investigations give the possibility of predicting useful life time of materials.